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Auerbach Associates, Inc, Philadelphia, PA

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TASK V

BENZENE CONSUMPTION

AS A SOLVENT

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This study was conducted to determine the current status of the industrial and consumer consumption of benzene as a solvent, and to identify where possible any impact on its use as a solvent due to the OSHA Emergency Benzene Standard (42 FR 27452, May 27, 1977). The report presents an overview of the technical and commercial history of benzene and a discussion of its marketing and distribution patterns into the small miscellaneous use market. Consumption processes and patterns of benzene use, both before and after the OSHA regulations, are examined in detail. Consideration is given to the use of benzene in formulated products, such as adhesives and paint removers, and to benzene consumption as a solvent and adjunct to manufacturing in processes such as esterification and azeotropic dehydration. Possible alternatives to the use of benzene are explored. Losses of benzene to the environment are analyzed and an estimate of their geographic distribution is given.

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Market Input/Output Studies

Task V

Benzene Consumption as a Solvent

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FOREWORD

This study was conducted to determine the current status of the industrial and consumer consumption of benzene as a solvent, and to identify where possible any impact on its use as a solvent due to the OSHA Emergency Benzene Standards (42 FR 27452, May 27, 1977).

Approach to the Study

Since the consumption patterns for benzene as a solvent fall into two major areas (as an adjunct to chemical manufacturing processes and in the formulation of industrial and consumer products), it was necessary first to identify those companies which manufacture chemicals utilizing processes where benzene could be a solvent (esterification, azeotropic dehydration, extraction, recrystallization and reaction solvent uses), and manufacturing companies in the following areas: paints, coatings and paint removers, and solvent-type rubber-based adhesives.

Altogether 405 companies were identified and interviewed to determine the status of their use of benzene. They were identified through the use of appropriate trade and manufacturing directories and from our personal knowledge of the chemical manufacturing industry. A list of the companies contacted is presented in Appendix II.

In addition, a thorough search of the published literature was conducted to uncover any relevant consumption data.

Organization of the Study

The study is organized into five sections. Section I presents a general overview of the technical and commercial history for the manufacture of benzene. Section II discusses the marketing and distribution patterns of benzene into the miscellaneous or small volume use areas which constitute the basis of its consumption as a solvent. Section III examines in detail the consumption processes for the two major areas of benzene use as a solvent discussed above, presenting, where the information was available, patterns before and after the OSHA regulations. Section IV presents feasible alternatives to the use of benzene as a solvent, and Section V summarizes the losses of benzene to the environment with an estimation of their geographic distribution, as a result of the processes described in Section III.

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SECTION I. STATUS AND OUTLOOK SUMMARY

Benzene is a major raw material for the chemical industry. Almost all the benzene produced is converted into other chemical products. The small quantity remaining goes into inventory, export, or various miscellaneous commercial and industrial solvent applications.

With the growing concern over the health and environmental hazards of benzene and the increasing regulation of the amount permitted in the workplace, most small consumer-oriented uses of benzene, as a solvent in such products as paint removers, tire patch kits and rubber adhesives, have been eliminated.

Until the late 1950's, benzene was obtained chiefly as a by-product of coke manufacture. Petroleum-derived benzene entered the marketplace in the period 1940-1950. Since then, petroleum-derived benzene production has grown and today provides more than 90% of all benzene produced in the United States.

Since 1967, benzene production has shown an average annual growth rate of more than 5%. Annual changes in benzene production have varied from a decline of 31% between 1974 and 1975 to an increase of 39% between 1975 and 1976.

Benzene production appears to be sensitive to both the economic cycle and to the increasing demand for aromatics in unleaded gasoline. It is expected that the supply-demand situation for benzene will continue to follow past patterns.

1.1 OVERVIEW OF THE TECHNICAL HISTORY OF BENZENE

Originally, benzene was obtained only as a by-product of coke manufacture. With the rapid increase in demand for aromatics during World War II, petroleum refiners developed methods for the recovery of toluene and xylene from petroleum. As demand for benzene grew in the late 1940's, these processes were easily adapted for benzene production. 1950 was the first year that measurable quantities of petroleum-based benzene were produced. Within ten years, more benzene was being produced from petroleum than from coal. Today more than 90% of benzene production is petroleum-based (see Table 1-2).

Coke-oven benzene is isolated by fractional distillation of light oil recovered from coal gas derived from coking of coal. A small amount of light oil occurs as a fraction of by-product coal tar. About two gallons of benzene are recovered per ton of coal (Lowenheim and Moran, 1975).

There are three major petroleum sources of benzene: the catalytic reformate from refinery streams; pyrolysis gasoline, a by-product of ethylene manufacture; and hydrodealkylation of toluene (Fick, 1976). Nearly half of the supply of benzene is from refinery reformate. By 1985, this is expected to slip to only 38% of supply, although production from this source should exceed one billion pounds. Pyrolysis gasoline as a benzene source is forecast to account for a 31% share of production in 1985, spurred by projected increases in ethylene capacity (Fick, 1976) for the manufacture of polyethylene. Production of benzene from toluene depends on the markets for and relative prices of both chemicals. Hydrodealkylation is an expensive process, and is only profitable when there is a large price spread between toluene and benzene. The need for high octane unleaded gasoline could spur demand for toluene for this use, making it less available for conversion to benzene.

Table 1-1 shows the distribution of benzene supply sources for 1976, together with projections for 1985.

TABLE 1-1. BENZENE SUPPLY SOURCES
(Fick, 1976)

	1976*		1985	
	million gallons	%	million gallons	%
Refinery Reformate	710	48	1070	38
Pyrolysis Gasoline	155	10	880	31
Toluene Hydrodealkylation	450	30	550	19
Coal Processes	100	7	200	7
Imports	75	5	150	5
Total	1490	100	2850	100

---

* 1976 figures are estimates made during the first half of 1976, and as such will not correspond to official U.S. International Trade Commission data cited elsewhere in this report.

1.2 OVERVIEW OF THE COMMERCIAL HISTORY OF BENZENE

Benzene production, broken down by source, is shown for the last ten years in Table 1-2.

TABLE 1-2. U.S. PRODUCTION OF BENZENE (Millions of Gallons)
(U.S. International Trade Commission, 1975-1978;
U.S. Tariff Commission 1970-1974)

	From Coke Oven Operations	From Petroleum	Total	% Change
1968	92.6	907.5	1000.1	
1969	101.7	1083.6	1185.3	18.5
1970	93.5	1040.0	1133.5	-4.4
1971	72.1	1003.8	1075.9	-5.1
1972	79.8	1172.6	1252.4	16.4
1973	85.9	1367.4	1453.3	16.0
1974	82.1	1406.1	1488.2	2.4
1975	65.0	958.9	1023.9	-31.2
1976	60.4	1364.8	1425.2	39.2
1977(p)	--	---	1535.4	7.7

P = Preliminary

Benzene production has grown at an average rate of more than 5% per year since 1967. The most extreme annual changes occurred in the period 1974-1976. Production plummeted 31% in 1975, to the lowest level since 1968, and then rebounded in 1976, increasing 39% over the low of the previous year. This corresponds to the general economic recession in 1974 and 1975.

There are 41 producers of benzene, operating 57 plants. Estimated total capacity is 2,003 million gallons per year. Table 1-3 lists the producers with capacities by plant.

Benzene is the basic chemical building block for the aromatic chemical industry. Over 97% of the benzene produced in 1977 was converted into other chemical products. Estimated benzene consumption as a chemical intermediate has been calculated from published production statistics where available, or from the best available information from private sources. These estimates are presented in Table 1-4. In several cases, figures for derivative production were adjusted to account for non-benzene based sources.

The best available conversion factors were used to obtain benzene consumption from the production statistics for each derivative. They appear in Table 1-5. The conversion factors were assumed to be constant over the period studied (1971-1977). A density factor of 7.365 lbs./gal. of benzene was used to change pounds into gallons.

Calculations of benzene consumption are subject to much uncertainty. Inaccurate or incomplete reporting of production data to government and trade organizations is one source of error. Another is the selection of conversion factors, which may vary widely, as illustrated by the inclusion of factors from two different sources in Table 1-5. A small change in the conversion factor could have a large effect on the computed benzene consumption figure.

TABLE 1-3. ANNUAL CAPACITY OF BENZENE PRODUCERS
(Gunn and Ring, 1977; Private Industry Contacts, 1978)

Company	Plant Location	Capacity (MM gal.)
Amerada Hess Corp. Hess Oil Virgin Islands Corp.	St. Croix, VI	65
American Petrofina Inc. American Petrofina Co. of Texas	Port Arthur, TX	20
American Petrofina of Texas/Union Oil Co. of California (joint venture)	Beaumont, TX	22
Cosden Oil and Chemical Co.	Big Spring, TX	58
Armco Steel Corp.	Middletown, OH	3
Ashland Oil, Inc.	Ashland, KY	64
	North Tonawanda, NY	23
Atlantic Richfield Co.	Channelview, TX	32
Arco Chemical Co.	Houston, TX	42
	Wilmington, CA	12
Bethlehem Steel Corp.	Bethlehem, PA	4
	Sparrows Point, MD	15
CF&I Steel Corp.	Pueblo, CO	3
The Charter Co. Charter Oil Co., subsidiary Charter Chemicals- Charter International Oil Co.	Houston, TX	5
Cities Service Co.	Lake Charles, LA	25
Coastal States Corp.	Corpus Christi, TX	70
Commonwealth Oil Refining Co., Inc. Commonwealth Petrochemicals, Inc.	Penuelas, PR	185
Crown Central Petroleum	Pasadena, TX	23
The Dow Chemical Company	Bay City, MI	30
	Freeport, TX	50
Exxon Corporation	Baton Rouge, LA	70
Exxon Chemical Co., div.	Baytown, TX	60
Getty Oil Company	El Dorado, KS	13

TABLE 1-3. ANNUAL CAPACITY OF BENZENE PRODUCERS (cont'd)

Company	Plant Location	Capacity (MM gal.)
Gulf Oil Corp. Gulf Oil Chemicals Co., Div.	Alliance, LA	67
	Philadelphia, PA	37
	Port Arthur, TX	40
Independent Refining Corp.	Winnie, TX	3
Kerr-McGee Corp. Southwestern Refining Co., Inc.	Corpus Christi, TX	16
The LTV Corp. Jones & Laughlin Industries, Inc.	Aliquippa, PA	10
Lone Star Steel Corp. Subs. of Northwest Industries, Inc.	Lone Star, TX	1.4
Marathon Oil Company	Texas City, TX	7
Mead Corporation	Chattanooga, TN	0.2
	Woodward, AL	1.4
Mobil Corporation Mobil Chemical Co.	Beaumont, TX	60
Monsanto Company Monsanto Chemical Intermediate Co.	Alvin (Chocolate Bayou)/ Texas City, TX	85
Pennzoil Co. Atlas Processing Co.	Shreveport, LA	15
Phillips Petroleum Co. Phillips Chemical Co.	Sweeny, TX	10
Phillips Puerto Rico Core, Inc.	Guayama, PR	110
Quintana-Howell (joint venture of Quintana Refinery Co. and the Howell Corp.)	Corpus Christi, TX	7
Shell Oil Co. Shell Chemical Co.	Deer Park, TX	90
	Odessa, TX	12
	Wood River, IL	45
Standard Oil Co. of California Chevron Chemical Co.	El Segundo, CA	23

TABLE 1-3. ANNUAL CAPACITY OF BENZENE PRODUCERS (cont'd)

Company	Plant Location	Capacity (MM gal.)
Standard Oil Co. of Indiana Amoco Oil Co.	Texas City, TX	85
The Standard Oil Co. (Ohio) BP Oil Inc.	Marcus Hook, PA	8
Sun Company Inc.	Corpus Christi, TX	38
Sun Oil Company of Pennsylvania	Marcus Hook, PA	29
Sun Petroleum Products Co.	Toledo, OH	49
	Tulsa, OK	24
Tenneco Inc. Tenneco Oil Co.	Chalmette, LA	10
Texaco Inc.	Port Arthur, TX	45
	Westville, NJ	35
Union Carbide Corp. Chemicals and Plastics Div.	Taft, LA	70
Union Oil Co. of California	Lemont, IL	17
Union Pacific Corp Champlin Petroleum Co., subs.	Corpus Christi, TX	10
United States Steel Corp.	Clairton, PA	45
USS Chemicals	Geneva, UT	4
Total		2003

TABLE 1-4. ESTIMATED CONSUMPTION OF BENZENE AS A CHEMICAL INTERMEDIATE (1,000 Gallons)*
(AAI, 1977, 1978)

	1971	1972	1973	1974	1975	1976	1977
Ethylbenzene	535,686	688,125	692,310	689,931	534,687	720,605	780,685
Cumene	200,872	214,818	249,712	272,218	187,626	254,436	247,320
Cyclohexane	182,082	239,436	221,122	244,969	180,603	227,787	233,508
Aniline	44,723	50,080	55,924	67,354	49,727	66,450	71,374
Chlorobenzene, Mono-	45,527	44,925	44,254	42,217	34,072	36,638	36,741
Chlorobenzene, Di-	10,443	11,760	10,841	10,406	8,455	9,031	9,056
Alkylbenzene, Linear	29,875	28,459	27,060	28,938	26,897	28,713	28,520
Alkylbenzene, Branched	11,304	10,768	10,238	10,947	10,177	10,862	11,123
Maleic Anhydride	38,817	46,578	47,830	49,138	34,799	41,531	36,343
Phenol (from Benzene Sulfonic Acid)	14,802	16,357	15,259	14,287	13,339	16,293	16,483
Anthraquinone	9,473	10,257	10,088	10,084	7,901	10,048	10,048
Resorcinol	3,026	3,523	4,090	4,196	2,880	4,073	4,073
Biphenyl	2,854	3,321	3,853	3,948	2,716	2,716	2,783
Nitrobenzene (not for Aniline)	1,543	1,946	1,090	1,788	1,462	2,716	2,716
Hydroquinone	303	352	409	420	288	407	407
Total Consumption as Intermediate	1,131,330	1,370,705	1,394,080	1,450,891	1,095,629	1,432,306	1,491,180

* See Appendix I, Notes on Calculations

TABLE 1-5. CONVERSION FACTORS* FOR BENZENE CONSUMPTION

(Gunn and Ring, 1977; Lowenheim and Moran, 1975)

Derivative	Factor	
Ethylbenzene	0.76	(0.74)**
Cumene	0.69	(0.80)
Cyclohexane	0.93	(0.94)
Aniline	0.90	
Monochlorobenzene	0.82	(0.95)
Dichlorobenzenes	0.62	
Linear Alkylbenzene	0.40	(0.49)
Branched Alkylbenzene	0.40	
Maleic Anhydride	1.25	(1.34)
Phenol (from Benzene Sulfonic Acid)	(1.00)	
Nitrobenzene	(0.65)	

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* Pounds of benzene per pound of derivative

** Figures in parentheses ( ) are from Lowenheim and Moran; all others are from Gunn and Ring.

Seven major benzene derivatives accounted for 97.5% of benzene consumption in 1977, and have consumed more than 97% of the benzene produced since at least 1971. They are listed in Table 1-6.

TABLE 1-6. BENZENE CONSUMPTION FOR MAJOR CHEMICAL DERIVATIVES, 1977

(AAI, 1978, based on Table 1-4)

	% of Total Consumption
Ethylbenzene	52.4%
Cumene	16.6
Cyclohexane	15.6
Aniline	4.8
Chlorobenzenes	3.1
Alkylbenzenes	2.6
Maleic Anhydride	2.4
	97.5%

The remaining benzene is consumed by the manufacture of smaller-volume derivatives (see lower part of Table 1-4), miscellaneous uses, changes in inventory, and net exports. The miscellaneous uses of benzene, which take up a very small portion of the total consumption, include the synthesis of a wide variety of speciality chemicals, use as an adjunct in the manufacture of chemicals, petrochemicals and polymers, and as a solvent in formulated products.

Inventory data, obtained from the National Petroleum Refiners Association (NPRA), are incomplete. Where available, they represent only the amount reported by those benzene manufacturers and major benzene consumers who submit data to the NPRA. For example, the 1976 inventory contained data from one company that did not report in 1975. This omission is estimated to amount to as much as 50 million gallons. The data also do not include benzene held in storage by brokers, resellers, or smaller benzene consumers. Inventory data for five years are shown in Table 1-7.

TABLE 1-7. BENZENE INVENTORY DATA
(National Petroleum Refiners Association, 1977, 1978)

	Benzene in Inventory as of Dec. 31 (gal.)	Change in Inventory Compared to Previous Year (gal.)
1977	192,943,000	-17,003,000
1976	209,946,000	92,247,000
1975	117,699,000	-55,000,000
1974	172,699,000	86,145,000
1973	86,554,000	

An overall supply/demand summary of the benzene market based on Table 1-4, published information, and industry sources is presented in Table 1-8, and illustrated for 1977 in Figure 1-1. The table shows an approximate material balance for benzene and is not intended to provide a concrete numerical assessment of benzene availability and demand. The next to last row of the table, the difference between total available benzene and total consumption, is subject

TABLE 1-8. SUPPLY/DEMAND SUMMARY OF THE BENZENE MARKET (1,000 Gallons)
(AAI, 1978)

	1971	1972	1973	1974	1975	1976	1977
Total Benzene Production	1,075,900	1,252,400	1,453,300	1,488,200	1,023,900	1,425,200	1,535,400
Imports	76,687	95,965	51,867	102,258	70,320	52,523	61,346
Total Benzene Available	1,152,587	1,348,365	1,505,167	1,590,458	1,094,220	1,477,723	1,596,746
Consumption (Table 1-4)	1,131,330	1,370,705	1,394,080	1,450,891	1,095,629	1,432,306	1,491,180
Exports	42,589	29,002	29,610	23,453	18,300	28,917	26,834
Total Benzene Consumption	1,173,919	1,399,707	1,423,690	1,474,344	1,113,929	1,461,223	1,518,014
Difference: Available-Consumed	-21,332	-51,342	81,477	116,114	-19,709	16,500	78,732
Inventory Change				86,145	-55,000	92,247	-17,003

Sources: Production data, Table 1-2; Import and Export statistics, Bureau of Census, U.S. Dept. of Commerce, 1972-1978; Consumption figures, Table 1-4; Inventory, Table 1-7.

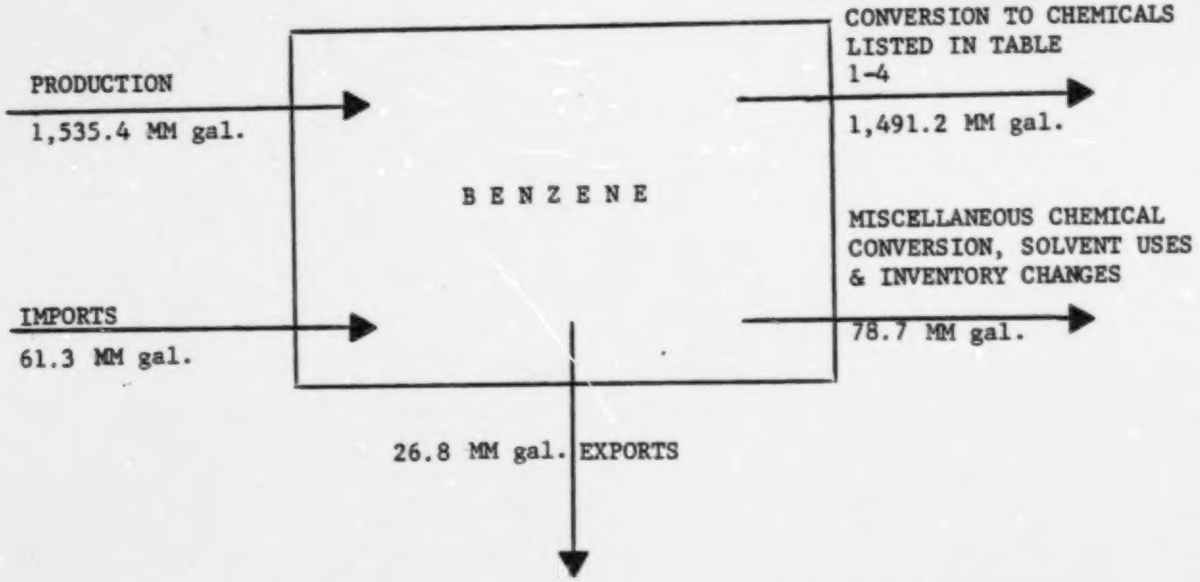

CONVERSION TO CHEMICALS LISTED IN TABLE 1-4
PRODUCTION
1,535.4 MM gal.
1,491.2 MM gal.
BENZENE
MISCELLANEOUS CHEMICAL CONVERSION, SOLVENT USES & INVENTORY CHANGES
IMPORTS
61.3 MM gal.
78.7 MM gal.
26.8 MM gal. EXPORTS

Figure 1-1. Input/Output Summary of Benzene Consumption, 1977

to uncertainty, due to the reporting and calculation errors in the figures which make it up (see earlier discussion of inventory data and conversion factors).

There is considerable variation in the material balance difference from year to year. Inclusion of annual inventory changes in the table does little to minimize this variation. As noted earlier, the calculation errors in determining benzene consumption and reporting errors of production are large enough to account for the entire difference between benzene availability and consumption (see final rows of Table 1-8).

The small volume of benzene consumed in the miscellaneous market is included in these difference figures. The miscellaneous market includes a range of consumer and industrial applications, such as:

(1) Conversion to small volume specialty organic chemicals

(2) Use as an adjunct in chemical manufacturing processes; e.g., as an azeotropic agent or extraction solvent

(3) Use as a denaturant for ethyl alcohol

(4) Use as a solvent in the formulation of consumer products, such as paint removers and rubber-based adhesives.

According to industry sources, the amount of benzene that enters this market is extremely small, probably on the order of three to five million gallons or less per year.

Benzene use as a solvent in consumer products such as paint removers and strippers, tire patch and retread adhesives, and rubber cements is reported to have dropped to near zero as a result of the Occupational Safety and Health Administration's emergency temporary benzene standard of May, 1977 (OSHA, 1977), which reduced the allowable concentrations of benzene in the workplace. This action also caused major benzene sellers and resellers to withdraw from the drum and small volume sales market. In addition, the Consumer Product Safety Commission has recently (May 19, 1978) issued a ban on the use of benzene in consumer products (Federal Register, 1978). This could lead to the total elimination of benzene from the formulations of consumer goods. The majority of consumer products have already been reformulated to eliminate benzene. In those cases where benzene is present, it is as an accidental contaminant in alternative solvents. Benzene does find some use as a denaturant of alcohol. Currently, however, its most widespread miscellaneous use occurs in chemical manufacture, where it is used both as a chemical intermediate for specialty chemicals and an adjunct.

Benzene is sold through manufacturers, distributors and resellers. Large bulk sales are handled by producers and distributors having appropriate terminals from which it is moved by pipeline, barge, railroad tank car or tank truck. Smaller sales, in tank wagon or drum quantities, are made by distributors and resellers.

As a result of the OSHA ruling, many of the larger benzene distributors and resellers have discontinued small volume drum sales. Nearly all of the smaller solvent dealers have stopped handling benzene. A few "can get" benzene, but will not store, handle or drum it themselves.

SECTION II. GENERAL MARKETING AND DISTRIBUTION PATTERNS

The sales and distribution patterns for the miscellaneous markets of benzene have been affected by the OSHA temporary standard, resulting in a strong trend away from small volume benzene handling (drums and spot sales in bulk) among suppliers. Benzene manufacturers and large bulk solvent distributors are discontinuing all but large volume bulk sales, which are generally to chemical manufacturers for intermediate use. Smaller distributors and solvent blenders are eliminating benzene sales which require storage and repackaging. Many have discontinued all sales of benzene. Some customers who still want benzene for their processes have reported difficulties in obtaining the small quantities they require.

2.1 PRODUCERS

The producers of benzene, which include steel (coke) manufacturers and petroleum refiners, are geared to high volume bulk sales and distribution. These companies report sales in tankcar, barge and pipeline quantities to "major consumers", who are generally either large regional distributors or chemical companies who use the benzene as a chemical intermediate in the production of derivatives such as styrene. None of the suppliers in this group deal in quantities smaller than carloads or truckloads. However, some of the companies that produce benzene are equipped to deal in the occasional tankcar and tankwagon volumes required by small users.

Since these large producers sell the bulk of their benzene directly to chemical manufacturers or regional distributors they make little direct contribution to the small volume miscellaneous use market.

2.2 LARGE BULK DISTRIBUTORS

Some benzene enters the miscellaneous use market from large bulk distributors, many of whom have shipping terminals and offices nationwide. They sell benzene directly in tankcar and tankwagon quantities, as well as in larger quantities (via barge and pipe line) to major consumers, and to distributors.

The companies in this group handle large volumes of benzene and other solvents, both in bulk and in small lots. In recent years, and especially since the May, 1977 OSHA ruling, these companies have been moving away from small volume (drum) benzene sales. Two of the national distributors contacted have discontinued handling benzene in their terminals.

Table 2-1 presents a representative view of the consumption patterns of benzene based on interviews with 13 major distributors. For several of these companies the distinction between "producer" and "large distributor" is difficult to make. This table does not attempt to account for all benzene entering the miscellaneous use market; however, the drop to approximately 25% of the sales volume prior to 1977 agrees with the general trend as reported elsewhere in this study.

Current benzene distribution can be characterized as follows. The large producers pipeline or barge benzene in bulk to large chemical consumers or to major distributors, who have strategically located bulk terminals. From the major distributors it would be shipped in bulk (tankwagon or tankcars) to regional distributors or local solvent resellers and formulators, or directly to regional end users. The large producers and distributors have discontinued all

TABLE 2-1. BENZENE SALES VOLUMES OF LARGE DISTRIBUTORS TO THE MISCELLANEOUS USE MARKET

Company	Annual Volume Sold Pre-OSHA (1976) (gallons)	Annual Volume Sold Post-OSHA (1977) (gallons)	Customer type/Comments
A	100,000-125,000	100,000-125,000	1-2,000 gallons in drums but do not drum themselves
B	minimal tank wagon sales	bulk sales only 200,000	aluminum alkyls (170,000) a national solvent distributor
C	direct bulk sales only	direct bulk sales only	chemical intermediate
D	50,000 tank wagon lots to local distributors	bulk sales only	reseller
E	direct bulk sales only	direct bulk sales only	
F	bulk sales	bulk sales	chemical intermediate
G	shipload sales only	shipload sales only	
H	200,000 (90% of small sales to paint industry)	140,000 (Al. Alkyls) 10,000 (Misc. uses)	aluminum alkyls; ceased drumming operations
I	800,000	discontinued sales to small consumers	
J	100,000	discontinued handling benzene at all 30 locations	
K	1,000,000	bulk sales only	
L	not available	290,000	alkyls and tetraethyllead; 25,000 purchased for drumming
M	200,000	not available	paint remover (discontinued 1978); insecticide manufacturer; tire patch kits
Estimated Total	2,450,000	740,000	

drumming facilities, and many regional bulk terminals have been eliminated. A few of the large producers are continuing to make "spot" or non-contract bulk sales of benzene.

2.3 FORMULATORS AND BLENDERS

In the past, benzene has been sold as a component of solvent and paint stripper blends. All of the eight formulators contacted reported no longer using benzene in their blends. Benzene use was halted as much as four to six years ago in some cases, while in others, use was discontinued as recently as the May, 1977 OSHA ruling. Chlorinated solvents and other solvents considered less hazardous than benzene have been substituted in the solvent blends. Benzene consumption in solvent blends is given in Table 2-2 for those companies providing data. Section 3.5 contains a complete discussion of benzene use in the paints and coatings industry.

According to one company's spokesman, the OSHA regulations have increased costs to the company in areas such as the handling and drumming of benzene, equipment, and insurance. Small companies are hit harder by the standard than are larger ones. The spokesman stated that his company may cease handling benzene regardless of customer demand.

2.4 SMALL DISTRIBUTORS

The majority of the benzene that enters the small volume market is handled by regional or local solvent distributors and resellers. Sales have been in drum lots, with individual companies generally selling a few thousand gallons a year each, although several reported annual turnovers of 10-15,000 gallons or more. Of the 54 small solvent distributors contacted, over half (29) said they had never carried benzene, had discontinued handling it more than four years ago, or simply that they did not now sell benzene. Another 17 discontinued handling benzene within the past 18 months. A few of these said they could get benzene, although it was not an active item. Only eight companies were identified as currently selling benzene.

TABLE 2-2. BENZENE CONSUMPTION OF SOLVENT BLENDERS

Company	Annual Volume Used in Solvent Blends - Pre-OSHA (1976) (gallons)	Annual Volume Used in Solvent Blends - Post-OSHA (1977) (gallons)	Customer Type/Comments
A	10,000	Nil	Formulated paint stripper, was 20% benzene. Benzene eliminated several years ago.
B	15-20,000	Nil	Formulated paint stripper
C	5,000	Nil	Formulated paint stripper
D	8-10,000	Nil	Sales to paint companies for formulation into strippers and thinners
E	≤5,000	Nil	Drum sales to paint companies
Total	43,000-50,000	0	

Table 2-3 summarizes benzene sales before and after the May, 1977 OSHA ruling for those small distributors who supplied sales information.

Among small volume distributors, there has been a strong movement away from benzene sales. The hazards of handling benzene and the expense of compliance with the OSHA standard and other local pollution and health regulations, combined with the sharp decline in demand for the solvent, have caused many companies to discontinue small sales of benzene.

2.5 TRANSPORTATION

The OSHA benzene standard will have an effect not only on the processing, handling and distribution of benzene, but on its transportation as well. An estimated 500-600 workers are involved in benzene transport by barge, railcar and truck. To meet the standard, improvements and changes in equipment and procedures may be necessary (Chemical Week, 1977). Another consideration in the movement of benzene is the growing concern over the safe transport of hazardous chemicals. Insurance problems, regulatory action and need for equipment modifications may all have an effect on the transportation of benzene.

Most miscellaneous market shipments of benzene are in tank trucks, compartmentalized trucks and drums. Several trucking companies were contacted concerning their transporting of benzene. Only one trucker reported refusing to haul benzene, as a result of the OSHA ruling. They had worked together with a major oil company trying to meet the standards. When they found they could not, they discontinued handling benzene, rather than invest in closed loading systems and equipment.

TABLE 2-3. BENZENE SALES VOLUMES OF SMALL DISTRIBUTORS

Company	Annual Volume Sold - Pre-OSHA (1976) (gallons)	Annual Volume Sold - Post-OSHA (1977) (gallons)	Customer Type/Comments
A	<4,000	Nil	Paint remover, adhesives
B	6,400	60 gal sold, last 9 months of 1977	Most sold in drums, but some in blends; company discouraging benzene sales
C	20,000	10,000 gal/yr. to one customer	Will still drum, but not store benzene
D	27,500 (1973)	6,600	Pints and gallons for lab use, paint and adhesives industries
E	13-14,000	(13-14,000)*	For use as extraction solvent, chemical intermediate (specialty)
F	13-20,000	(13-20,000)	Adhesives, fine chemicals
G	X**	will sell in tank cars	Will not sell drums. Use: industrial and specialty coatings
H	X	occasional partial tank wagon (500 gallons)	Alcohol denaturant, paints and coatings Do their own drumming Sales have dropped since OSHA ruling

* Pre-OSHA volume inserted in parentheses for companies not reporting current volumes, but considered to be still handling benzene.

** X = no volume reported

TABLE 2-3. BENZENE SALES VOLUMES OF SMALL DISTRIBUTORS (continued)

Company	Annual Volume Sold - Pre-OSHA (1976) (gallons)	Annual Volume Sold - Post-OSHA (1977) (gallons)	Customer Type/Comments
I	6,000	(6,000)	Paint remover (industrial) sold in drums
J	1 tank car load, in drums	(1 tank car load)	Sales low since shortage of 1973
K	X	about 1 drum in the past 18 months	Said they can get benzene if required
L	≤3,000	Nil	Sales were in drums for paint remover and rubber cement
M	2,500	Nil	Sales were for paint removers; will no longer drum benzene
N	7-10,000 mid-1976-mid-1977	Nil	Sales were for adhesives and paint removers Will sell bulk quantities, but will not store or handle; none in drums
O	12,000	Nil	Furniture strippers; sold in drums
Total	120,400-131,400	55,215-63,215	

Another company has felt no effects from the OSHA regulation. Their transport of benzene has always been erratic, fluctuating with the supply of rail tankcars. Because of this, they have no real way of knowing how the benzene market is faring under OSHA. The spokesman added that if the permanent standard goes into effect, everyone would have to convert to closed loading systems. So far, however, his company has not invested in any such equipment.

A third trucker has experienced no drop in benzene hauls in the Northeast since the OSHA emergency standard, and is running at about the same level of activity as last year. The spokesman for another trucking company estimated that the benzene standard has cost his trucking firm between $100,000 and $150,000. This includes the costs of monitoring, safety instruction and dedicated tank trailers where required.

The OSHA regulation will lead to increased costs for the transportation of benzene, brought about by equipment modifications, insurance and safety surveillance needed to meet the standard.

SECTION III. CONSUMPTION PROCESS STUDY

The consumption patterns for benzene's solvent and miscellaneous uses are reviewed in Section I. Benzene's basic use in the chemical industry is as an intermediate in the manufacture of a wide variety of chemicals (see Table 1-4), which consumes over 98% of the benzene produced. The balance is distributed between inventory, specialty chemical manufacture and a number of miscellaneous solvent uses.

The environmental exposure to benzene occurs in several ways:

(1) Fugitive escape during production and transportation

(2) Fugitive escape during the chemical conversion of benzene to other chemicals

(3) As a component of gasoline

(4) As a solvent in consumer and industrial products or fugitive escape during its use as an adjunct in chemical processes where it does not enter into a chemical reaction

There have been a number of studies on benzene production processes and its consumption in the production of other chemicals. Studies on its use in gasoline have also been made. Because of the fragmented nature of the solvent applications of benzene, these uses have often been considered to be a part of the "other uses" in input-output balances previously made. Neither the exact amount of benzene that is used as a solvent nor a detailed breakdown of its uses and losses has been known with any degree of accuracy.

This section addresses itself to a study of the quantity and uses of benzene as a solvent. There are two principal areas in which benzene is used exclusively as a solvent:

(1) As an adjunct in chemical manufacturing processes

(2) For the formulation of industrial and consumer products

The results of this study indicate that the benzene demand for use as a solvent does not exceed five million gallons. Although this is a small volume compared to the availability of benzene (less than 0.5%), it represents a significant potential loss of a hazardous chemical to the environment. This study, therefore, was undertaken to assess the potential hazard to health and environment resulting from this use of benzene.

The solvent uses of benzene by industry are numerous. The quantity consumed by any one processor varies from as little as 200 gallons per year to as much as 500,000 gallons per year. Because the quantity per user is small, it was necessary to interview a very large number of companies who might be solvent users to ascertain:

(1) Their present and past benzene consumption

(2) The influence of the OSHA Emergency Benzene Standard on benzene consumption

(3) Alternate solvents

(4) Methods of control and disposal of benzene emissions and wastes

(5) Where possible, the actual environmental losses.

Figure 3-1 illustrates the miscellaneous uses of benzene as a solvent that have been considered in the preparation of this study.

3.1 ADJUNCT IN CHEMICAL PROCESSES

A wide variety of solvents is used in chemical manufacture and chemical processing for the following operations:

(1) As an azeotroping agent for water removal (dehydration)

(2) As a reaction solvent or reaction medium

(3) As an extracting agent to separate product from the reaction mass

(4) As a recrystallizing agent to remove impurities from the product.

These operations are widespread in the chemical industry, and are used in the following sectors:

(1) Pharmaceuticals
(2) Fine Chemical Manufacture
(3) Flavors and Fragrances
(4) Botanicals
(5) Pesticides
(6) Synthesis of Esters
(7) Anhydrous Alcohols (ethyl and propyl)

Each of these sectors covers a multitude of chemicals. Considerable proprietary information would have to be obtained if process solvent uses were to be correlated with the manufacture of an individual chemical. Specific chemicals for which sufficient data could be obtained are discussed in separate parts of this section. These include:

(1) Aluminum alkyls
(2) Ethyl cellulose
(3) Alcohol manufacture, including denaturing of ethyl alcohol
(4) Bisphenol-A

Benzene has a long history of use as a solvent in chemical manufacture because of its relatively high volatility (low boiling point), strong solvent properties for many organic materials, and insolubility in water.

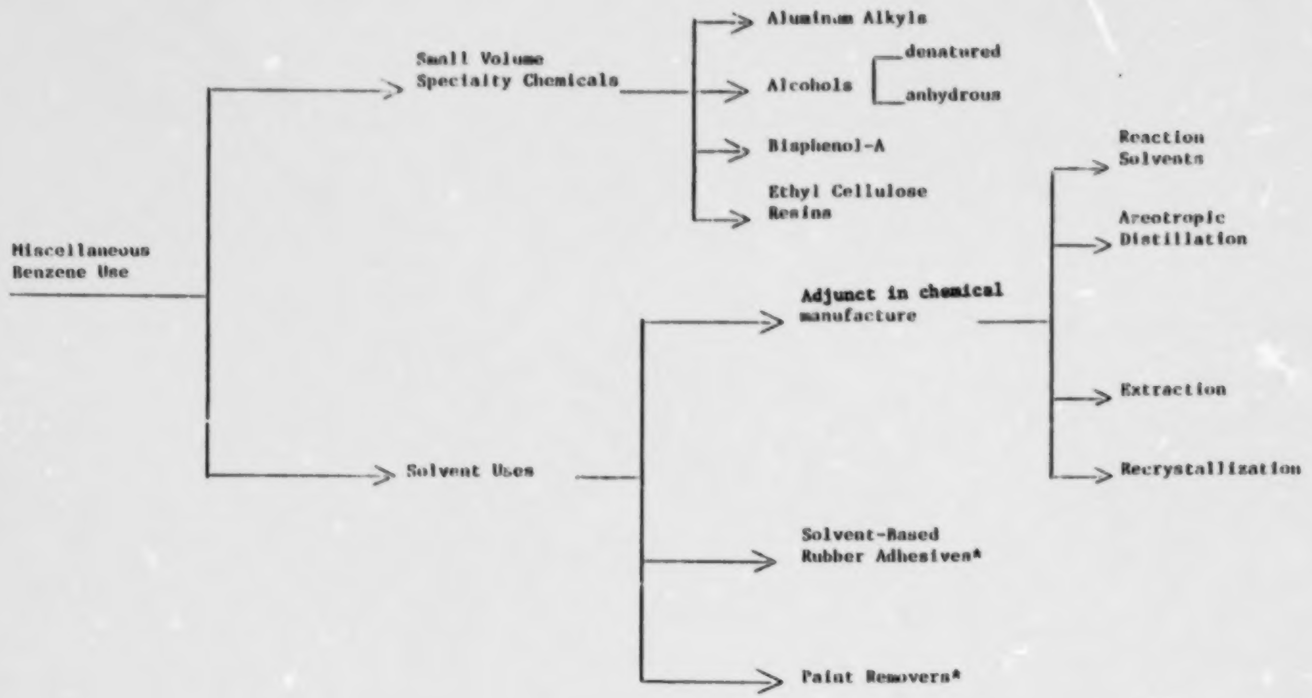

Miscellaneous Benzene Use
Small Volume Specialty Chemicals
Aluminum Alkyls
Alcohols
denatured
anhydrous
Bisphenol-A
Ethyl Cellulose Resins
Solvent Uses
Adjunct in chemical manufacture
Reaction Solvents
Azeotropic Distillation
Extraction
Recrystallization
Solvent-Based Rubber Adhesives*
Paint Removers*

Figure 3-1. Miscellaneous Benzene Uses, 1976

* As of 1977, benzene has been substantially eliminated from these products.

In addition, benzene has sold at a lower price than other comparable solvents and has been readily available.

Benzene consumption as a solvent for chemical manufacture has been decreasing over the years primarily because of its toxicity and increases in price which have eroded any cost advantage that it may have had over other solvents. This trend has accelerated following the promulgation by OSHA in May, 1977 (OSHA, 1977) of a regulation restricting the use of benzene in the workplace.

The Standard Industrial Classification (SIC) classifies the chemical industry as follows:

281: Industrial Inorganic Chemicals
282: Plastic Materials and Synthetics
283: Drugs
284: Soaps, Cleaners and Toilet Goods
285: Paints and Allied Products
286: Industrial Organic Chemicals
287: Agricultural Chemicals
289: Miscellaneous Chemical Products

In this section, the potential for benzene use as a solvent in the manufacture of chemicals will be studied for the following classes:

282: Plastic Materials and Synthetics
283: Drugs
286: Industrial Organic Chemicals
289: Miscellaneous Chemical Products

Section 285, Paints and Allied Products will be reviewed in Section 3.3.3. A review of the processes used in the manufacture of products covered by industrial classifications 281, 284 and 287 indicated that benzene solvents are not used as an adjunct in their manufacturing processes.

3.1.1 General Organic Synthesis

Benzene is one of many solvents used as an adjunct to the manufacture of a large number of organic chemicals. The industrial classifications which encompass the bulk of these applications are:

2869:	Industrial Organic Chemicals, N.E.C.
282 :	Plastic Materials and Synthetics
283 :	Drugs

A discussion of the use of benzene in the manufacture of pharmaceutical chemicals (SIC 283) will be found in Section 3.1.2.

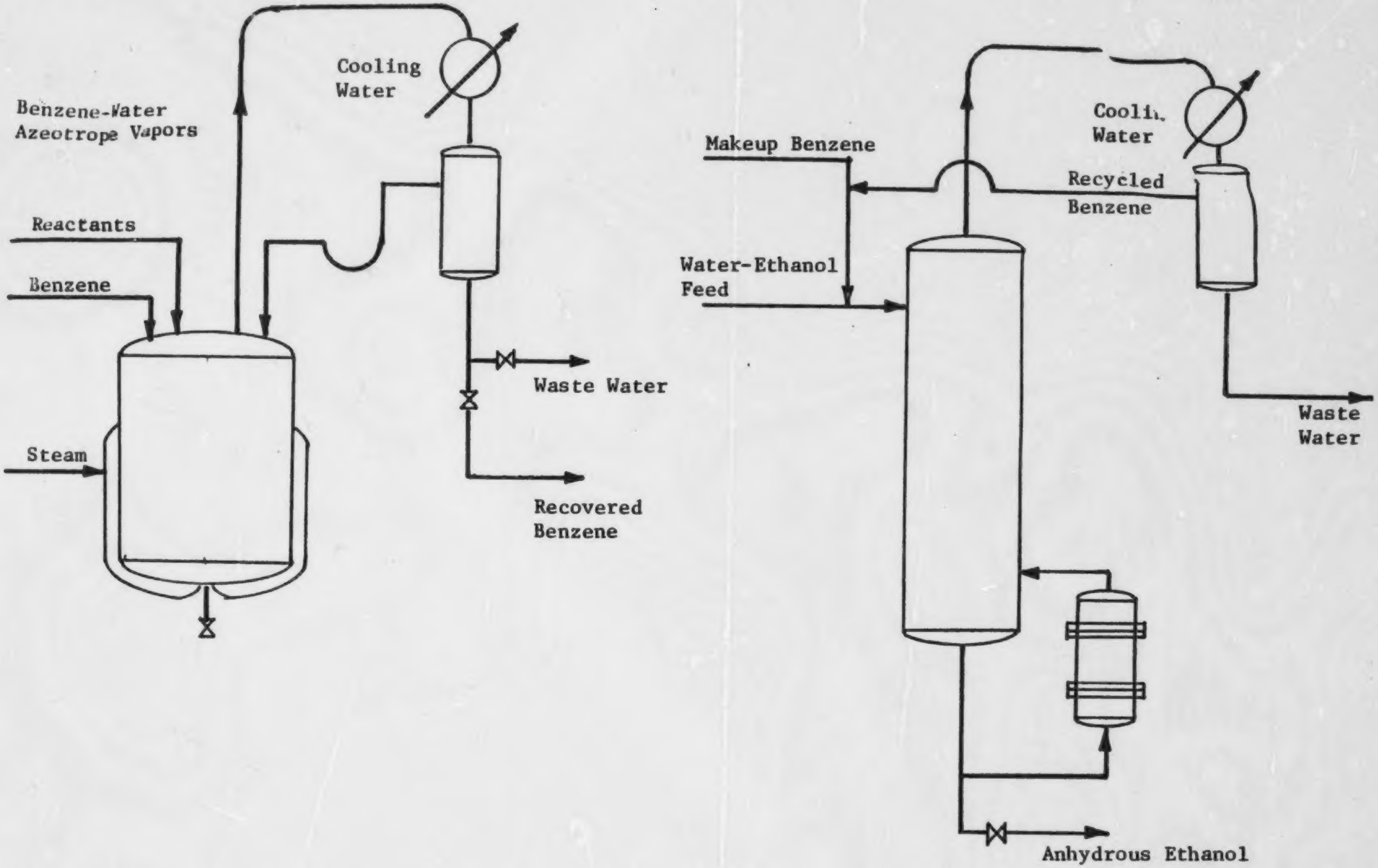
Solvents are used in the polymerization of certain polymers and synthetic rubbers (SIC 282). In these processes benzene finds limited use both as a catalyst carrier and reaction solvent. This application will be discussed in Section 3.2.1.

3.1.1.1 Process Description

Process operations in which benzene is used as a solvent vary widely with the chemical manufactured. In a typical azeotropic dehydration process in which water is removed (e.g., esterification reactions or production of anhydrous ethanol), the benzene is added to the reactants in a distillation apparatus, and heat is applied to boil the water-benzene azeotrope. The resulting vapors are condensed, the condensate flows to a decanter where benzene is removed as a top layer and returned to the distillation unit; the water saturated with benzene is removed for disposal.

When all the water is removed from the reaction mixture, the benzene is distilled and recovered for reuse. Process flow diagrams for typical azeotropic distillation processes are shown in Figure 3-2.

Extraction processes requiring the use of solvents as an adjunct to chemicals manufacture are common to chemical operations. They find application in the purification of chemicals and recovery of intermediate or end products from a reaction mass.


Benzene-Water
Azeotrope Vapors
Cooling
Water
Reactants
Benzene
Steam
Waste Water
Recovered
Benzene
Makeup Benzene
Water-Ethanol
Feed
Cooli
Water
Recycled
Benzene
Waste
Water
Anhydrous Ethanol

Batch Esterification Process or
Reaction in Presence of Solvent

Continuous Azeotropic Ethanol
Dehydration Process

Figure 3-2. Typical Azeotropic Distillation Processes

In extraction processes, benzene is mixed with the reaction mass which contains the desired component dissolved in a liquid immiscible with benzene. The benzene extracts (dissolves preferentially) the desired chemical. The resulting solution is separated by decantation followed by distillation where the benzene is vaporized and recovered, leaving the desired component as a residue. Alternately, the benzene extract may be fed to a reactor for further reaction. The benzene solvent is recovered by distillation.

In purification operations, the benzene may be used to recrystallize a material, leaving the impurity in solution from which the benzene is then recovered by distillation.

Process flow diagrams for typical batch extraction and recrystallization (purification) processes are shown in Figure 3-3.

3.1.1.2 Process Consumption

According to the Census of Manufactures for 1972, there were 514 establishments (sites) which reported the manufacture of chemicals under SIC 2869. Of these, 295 had 20 or more employees. Since chemical companies may manufacture industrial organic chemicals at more than one site, the number of establishments may not be equated to the number of companies. We have assumed that companies employing more than 20 people are the only ones that could manufacture chemicals at more than one site. On this basis, it is estimated that there are about 367 companies* which manufacture products under SIC 2869.

For this portion of the study, 142 companies who synthesize organic compounds were interviewed. Thirty-six companies (25%) representing about 41 establishments, reported that they used or were using benzene as a solvent material within the past five years; the remaining 106 companies used alternate

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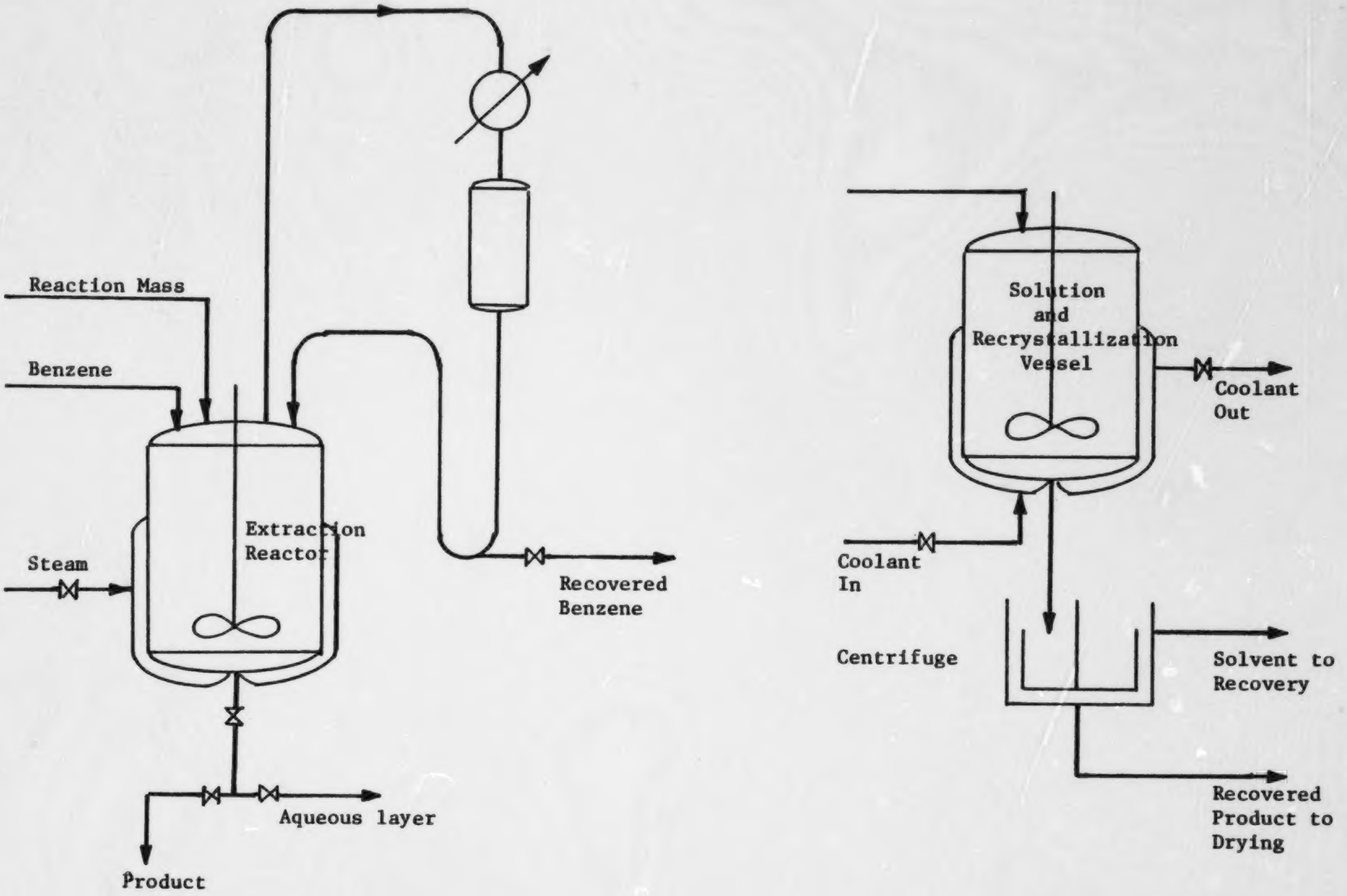
* It is assumed that the average number of sites per company with over 20 employees is two; the 295 "large" sites therefore represent 148 companies. Each of the smaller employment sites represents one company for a total of 514 - 295 = 219 companies; 219 + 148 = 367 potential companies who manufacture under SIC 2869.


Reaction Mass
Benzene
Steam
Extraction Reactor
Recovered Benzene
Aqueous layer
Product
Solution and Recrystallization Vessel
Coolant Out
Coolant In
Centrifuge
Solvent to Recovery
Recovered Product to Drying

Extraction Processes

Recrystallization Purification

Figure 3-3. Typical Extraction Process and Recrystallization Purification Process

solvents or no solvents in their operations. Only two of the thirty-six companies reported they had discontinued benzene use prior to 1976. Fifteen of the thirty-six user companies reported they were no longer using benzene as a solvent in their operations as of May 1978 one company eliminated its use at one of its process sites, while one other reduced its consumption. The companies which eliminated benzene in their process are now using alternate materials.

Benzene consumption by company varies from 570,000 gallons to as little as 300 gallons. Site consumption is considerably less since the large benzene solvent users have more than one manufacturing site.

Total annual consumption in 1976 by those companies contacted who reported use of benzene as a solvent ranged between 1.098 and 1.198 million gallons. This data is summarized in Table 3-1. In 1978, following the issuance of OSHA's benzene regulations, the annual consumption is expected to decline to between 813,800 and 885,750 gallons.

The average benzene consumption per company, based on the 142 companies contacted, was 8,000 gallons annually in 1976 and about 6,000 gallons in 1978. On the assumption that there are 367 companies (see footnote on previous page) which could have processes requiring a solvent as an adjunct, then the benzene solvent consumption in the U.S. for chemical processing is estimated to be 2,962,000 gallons in 1976, and projected to be 2,214,000 in 1978.

Company spokesmen stated that the trend in the chemical industry is to look for alternate solvents, and that the figure of 2.2 million gallons projected consumption in 1978 is expected to decline rapidly during the next three to five years. The decline is attributable to the emphasis on the toxicity of benzene and the limitations on the quantity to be permitted in the workplace by OSHA.

The consumption of benzene for solvent purposes represents make-up for system losses. Many of the companies interviewed reported that emission control systems were being used to reduce benzene and other chemical emission to the environment. The estimated amount of benzene consumed given in the preceeding paragraphs must not be equated to the quantity lost to the environment.

TABLE 3-1. BENZENE CONSUMPTION IN GENERAL ORGANIC SYNTHESIS (gallons/year)

Company	Discontinued Use Prior to 1976	1976	1978	Application
A		572,000	429,000	Azeotropic dehydration
B		50 to 100,000	50 to 100,000	Azeotropic agent Reaction solvent
C		150,000	150,000	Reaction solvent Azeotropic agent
D		75,000	75,000	Azeotropic agent Esterification
E		75 to 100,000	0	Reaction solvent Polymerization
F		20,000	20,000	Purification extraction Reaction solvent
G		20,000	20,000	Azeotropic distillation Reaction solvent
H		20 to 30,000	20 to 30,000	Azeotropic distillation Esterification
I		10,000	0	Reaction solvent
J		11,000	1,000	Azeotropic dehydration
K		5,000	5,000	Solvent recovery and Resale
L		5 to 10,000	5 to 10,000	Azeotropic distillation Esterification
M		5 to 8,000	0	Azeotropic dehydration
N		6,600	0	Reaction solvent
O		6,800 to 13,700	6,800 to 13,700	Reaction solvent
P		5,000	0	Azeotropic distillation

TABLE 3-1. BENZENE CONSUMPTION IN GENERAL ORGANIC SYNTHESIS (gallons/year) (continued)

Company	Discontinued Use Prior to 1976	1976	1978	Application
Q		2,500	2,500	Azeotropic agent Esterification
R		2,000	0	Reaction solvent
S		2,000	2,000	Purification, extraction
T		1,300	0	Purification, extraction
Other	8 to 9,000	54,300	27,500	
Total		1,098,500 to 1,198,400	813,800 to 855,750	

3.1.1.3 Environmental Losses

Losses from solvent use of benzene in chemical processes may occur as a result of air emissions, waste water discharges or by disposal of solid wastes. Air emission losses are directly attributable to:

(1) Inefficient condensation of vapors in distillation processes
(2) Vaporization of benzene leakage from pumps and agitators, and from valves, flanges, etc.
(3) Drying of solids
(4) Venting of storage and process tanks.

Liquid losses result from:

(1) Solubility in water removed as an azeotrope with benzene
(2) Contaminated liquid waste products obtained from distillation, or extraction.

Solid losses result from:

(1) Residue in filter cakes
(2) Residue in extracted solids (e.g., botanicals).

The quantity lost from process operations varies from 1% of the total volume of solvent circulated through the system to 100% in those instances where benzene cannot be separated readily from waste materials, or the volume of benzene is too small for economic recovery.

None of the reporting companies were able to provide data on the amount of benzene actually lost via any specific route (air, liquid or solid). This was due to the relatively small volume of benzene lost from a specific process. For example, a loss of 10,000 gallons per year is equal to about 0.023 gallons/minute or 0.151 pounds/minute. If this quantity were vaporized, this would be equivalent to 1.0 cubic ft. per minute. For most operations, losses are probably divided equally between vapor emissions (to the atmosphere) and waste water losses.

The amount of benzene lost to the environment was determined from a review of the emission control information reported by the companies interviewed. The controls used included incineration of collected vent gases, incineration of liquid wastes, biological treatment of water effluents and approved solid waste disposal methods.

Table 3-2 presents our best estimate of the probable net loss to the environment of benzene when used as a solvent adjunct to the manufacture of chemicals. Extrapolation to the total environmental loss for the General Organic Synthesis industry was made by direct proportion, based on analysis of the data obtained from the companies interviewed and the total number of companies in this group (see footnote, page 31).

TABLE 3-2. ESTIMATED BENZENE SOLVENT LOSS TO ENVIRONMENT FROM CHEMICAL MANUFACTURE (1,000 gallons)

For Companies Directly Contacted	1976	1978 (projected)
Total Consumption	1,098 to 1,198	814 to 886
Estimated quantity destroyed in pollution control systems	842 to 927	704 to 764
Net loss to environment	262 to 277	110 to 122
Extrapolation for Total General Organic Synthesis		
Total extrapolated consumption	2,962	2,214
Estimated quantity destroyed in pollution control systems	2,271	1,915
Net estimated loss to environment	691	309

3.1.2. Pharmaceutical Industry

The pharmaceutical industry, as defined in the SIC 283, is composed of companies whose operations range from reselling formulated pharmaceuticals manufactured by other firms under private labels, to companies who synthesize, formulate and market their own pharmaceutical products.

Except for certain large volume chemicals such as aspirin, citric acid, and various fermentation products, most pharmaceutical synthesis is done in small (100 or 200 gallon capacity) batch-type reactors. Consequently, chemical production volumes are small, and solvent usage and accompanying losses would be correspondingly low.

According to the Statistical Abstract of the United States (1976), there were approximately 1,000 establishments classed as drug (pharmaceutical) companies (SIC 283) in 1972. Of these about 680 are classed in the subgroup 2834, Pharmaceutical Preparations, leaving approximately 400 establishments in subgroups 2831, Biological Products, and 2833, Medicinal Chemicals and Botanical Products.

The Census of Manufactures (1967) reported a total of 1,129 establishments in SIC 283. Of these, 125 or 11% were in SIC 2831 and about the same percentage in SIC 2833. It is within the SIC subgroups 2831 and, in particular, 2833 that are found companies with synthesis facilities "primarily engaged in (1) manufacturing bulk organic and inorganic medicinal chemicals and their derivatives; and (2) processing (grading, grinding and milling) bulk botanical drugs and herbs."

According to a 1970 compilation of 25,000 Leading U.S. Corporations (Newsfront, 1970), 90 companies that have sales ranging from one million dollars to over one billion dollars are listed in SIC 283. It is difficult to identify from published industry statistics those pharmaceutical companies which could have synthesis facilities (SIC 2831 and 2833) and those which are only formulators and processors of pharmaceutical preparations (SIC 2834). Many manufacturing pharmaceutical companies have been merged into larger firms with the result that for any given company, there may be one location at which chemical synthesis is performed and many locations at which formulation and packaging is done.

Several companies listed, e.g. American Cyanamid and Witco Chemical, are normally considered to be organic chemical manufacturers rather than pharmaceutical companies. The contribution of chemical synthesis to sales of most pharmaceutical companies is usually a small proportion of their business.

3.1.2.1 Process Descriptions

Pharmaceutical chemical manufacturing processes are identical with those used to synthesize general organic chemicals. The basic difference lies in the smaller equipment size and the relatively large number of steps required to produce a pure pharmaceutical chemical.

According to industry sources, processes which use solvents as an adjunct to pharmaceutical manufactuirng are almost identical to those required in general organic chemical manufacture as described in Section 3.1.1.1. These include:

Azeotropic distillation
Azeotropic dehydration
Extraction
Purification and recrystallization
Reaction solvent.

3.1.2.2 Process Consumption

For this section of the study, a list of 46 companies which could have facilities for chemical synthesis or botanical extraction was developed. From this list, twenty-eight companies or subsidiaries were contacted. Of these, ten companies reported some consumption of benzene as a solvent prior to May, 1977. Subsequent to this date, six companies substituted alternate solvents for benzene.

Prior to May 1977, the ten user companies (Table 3-3) reported benzene consumption in the range of 562,000 to 542,000 gallons per year. Current (May, 1978) consumption has dropped to the range of 213,200 to 214,200 gallons per year.

Companies such as Abbott, Merck, and Pfizer synthesize large quantities of organic and pharmaceutical chemicals for both merchant sale and captive use. In many respects the operation of this type of company is closer to that of organic synthesis manufacturers than pharmaceutical manufacturers. Generally, benzene solvent consumption by companies in this group is over 20,000 gallons each per year.

Typical pharmaceutical companies, such as Wyeth, Smithkline, Parke Davis, and Schering Corp., manufacture pharmaceutical chemicals on a smaller scale for captive use.

Because of the wide variation in benzene solvent uses between companies who manufacture pharmaceuticals and fine chemicals and those who manufacture only pharmaceuticals, an extrapolation of the data in Table 3-3 to the industry would have little validity. A more realistic approach to developing an average benzene consumption for the industry is to eliminate the few high volume consumers (over 20,000 gallons) and average the use by the remaining companies contacted. On this basis, the average benzene solvent use by any one pharmaceutical manufacturing company is calculated to be 2,370 gallons per year.* Extrapolating this figure, it is calculated that the probable consumption of benzene solvert by the entire pharmaceutical industry prior to May, 1977 was on the order of 40,000 gallons per year, exclusive of the 550,000 to 630,000 gallons per year reported by the five large users (i.e., over 20,000 gallons per company).

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* (Total to be excluded = 550,000 gallons, leaving 11,850 gallons to be averaged among five companies)

TABLE 3-3. BENZENE CONSUMPTION IN PHARMACEUTICAL MANUFACTURE
(Gallons per year)

Company	Consumption		Uses
	Pre-OSHA 1976	Post-OSHA 1978 (projected)	
A	60-70,000	4-5,000	Dehydration, azeotropes, crystallization
B	20-40,000	1,000	Reaction solvent in esterification (azeotropic solvent)
C	2,000	200	Product crystallization (purification and reaction solvent)
D	250 - 300,000 (multiple sites)	200,000	Reaction solvent, azeotropic dehydration, product crystallization
E	1,000	0	Azeotropic dehydration
F	20,000	0	Extraction of botanicals plus reaction solvent
G	200,000	0	Reaction solvent, azeotropic dehydration
H	550	0	Not reported
I	300	0	Not reported
J	8,000	8,000	Reaction solvent, azeotropic dehydration
Total	561,850 to 641,850	213,200 to 214,200	

Table 3-3 shows that current (May, 1978) benzene consumption as a solvent by the pharmaceutical companies interviewed is between 213,200 and 214,200 gallons per year. It is to be noted that all but one of the large users of benzene as a solvent have substituted other chemicals. Following the method of extrapolation discussed in the previous paragraph, the probable consumption of benzene in 1978 by the small users contacted, i.e., 13,200 gallons*, can be extrapolated to a total of 22,000-23,000 gallons annually for typical pharmaceutical companies. The total probable consumption for 1978 will be about 222,000 gallons.

3.1.2.3 Environmental Losses

Processes used in the manufacture of pharmaceutical chemicals are quite similar to those used in the manufacture of organic chemicals described in Section 3.I.1.3. Environmental losses from pharmaceutical manufacture are due to essentially the same sources described previously:

(1) Vent losses from distillation operations

(2) Venting of storage and process tanks

(3) Vaporization of leaks from mechanical equipment

(4) Drying of solids

(5) Water wastes from distillation operations

(6) Contaminated liquid wastes from distillation, recrystallization or extraction

(7) Residues in filter solids or extracted solids

There are no data which relate solvent losses in this industry as a percent of the volume in process. Since the quantities used are relatively small, there is a general consensus that percentage losses tend to be high, i.e. over 10%. Where in-process quantities are small, solvent recovery is usually not economic, nor is the installation of emission or waste liquid control systems. In such instances, contaminated solvents may be drummed for disposal by waste disposal companies.

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* Total to be excluded = 200,000 gallons, leaving 13,200 gallons to be averaged among the four companies

As is the case for general organic synthesis, the consumption of benzene solvent usually does not represent loss to the environment. The loss to the environment is the difference between the total loss from the process and the amount that is destroyed through the use of pollution control methods.

A review of the industry responses to our questions on environmental loss and environmental controls showed that very little control is exercised over air emissions, except for improvement in condensing efficiency.

Liquid waste effluent control generally consists of subjecting the contaminated waste water to at least a primary treatment. Other contaminated liquids (organics), which cannot be recovered by distillation are incinerated or, more often, sent to a commercial disposal company. There is no consensus as to the percent of benzene consumed by the pharmaceutical industry (i.e., process loss) as solvent make-up and lost to the environment, versus that which is destroyed.

One company noted that about 10% of the amount consumed was lost to the atmosphere. The balance were liquid losses. Of the liquid losses, about 22% was incinerated, another 22% was treated in secondary waste treatment systems, and the balance was sent as a dilute water solution to a municipal treatment system from which most of the contained benzene leaves without change. In other words, over 50% of the liquid losses could enter the environment as a component of waste water.

Most companies, including the one just discussed, believe that probably 70% of all benzene-containing liquid effluents are treated in such a way as to prevent their entering the environment, and within a few years, perhaps close to 90% will be treated.

On the basis that atmospheric loss represents 10 to 20% of the total consumed, and that 20 to 25% enters the water environment via waste water, it is concluded that between 30 and 40% of the benzene consumed as a solvent (make-up loss) by the pharmaceutical industry could enter the environment.

Table 3-4 gives a calculated estimate of the amount of benzene lost to the environment by the pharmaceutical industry, based on the previously estimated 30% environmental loss of the benzene consumed for process make-up.

TABLE 3-4. ESTIMATED BENZENE SOLVENT LOSS TO ENVIRONMENT FROM PHARMACEUTICAL MANUFACTURE (1,000 gallons)

Reporting Companies	1976-77	1977-78
Total Consumption	561.85 to 641.85	213.2 to 214.2
Estimated quantity destroyed in pollution control systems	393.3 to 449.3	149.2
Net Loss to Environment	169.55 to 192.55	63.96
Total Pharmaceutical Industry		
Total Estimated Consumption	601.85 to 681.85	222.00
Estimated quantity destroyed in pollution control systems	421.29 to 477.29	155.4
Net Loss to Environment	180.56 to 205.56	66.6

3.2 SMALL VOLUME SPECIALTY CHEMICALS

This section discusses a group of specialty chemicals whose production volume, although small, is sufficiently large to permit individual analyses of solvent uses of benzene. These chemicals were selected as potential users of benzene as a process solvent based on literature and industry references. The chemicals selected include aluminum alkyls, ethyl cellulose resins, alcohols, and bisphenol-A.

3.2.1 Aluminum Alkyls

Aluminum alkyls have been in commercial production in the United States since 1959. Although there are approximately 30 aluminum alkyls available in developmental and commercial quantities, the chief commercial products are triethylaluminum, trimethylaluminum and triisobutylaluminum.

3.2.1.1 General Description of the Industry

There are four domestic producers of aluminum alkyls, as shown in Table 3-5, but only Texas Alkyls (a division of Stauffer Chemical Co.) and Ethyl Corporation make merchant sales; the other two companies make these compounds for captive use. The producers of aluminum alkyls are large companies with a wide organic product range. There is also one small company that produces research and experimental quantities of aluminum alkyls.

TABLE 3-5. DOMESTIC PRODUCERS OF ALUMINUM ALKYLS
(AAI, 1978)

Company	Market
Ethyl Corp.	captive/merchant
Texas Alkyls	merchant
Hercules	captive
Conoco	captive

Aluminum alkyls are used as catalysts in Ziegler-type reactions to produce high density polyolefins such as polyethylene, polypropylene, 1,4-polybutadiene and in the Alfol process for manufacturing long-chain alpha-alcohols.

Domestic production (based on reports from the four producers) is estimated at about 157 million pounds annually.

Aluminum alkyls are shipped as the pure compound or dissolved in a suitable solvent. Solvent solutions are often requested by the consumers because: (1) aluminum alkyls are pyrophoric compounds which react violently when exposed to oxygen (the solvents help shield them from contact with oxygen) (2) the solvent is used by the consumer in his process as the reaction medium.

The hydrocarbon solvents most used as packaging mediums and their approximate consumption are shown in Table 3-6.

The choice of solvent is usually determined by the purchaser's process requirements, i.e., the packaging diluent is the same as the solvent used in the reaction and frequently supplies up to 100% of the process "make-up" solvent.

Industry sources stated that the benzene-aluminum alkyl blend all goes to one consumer who uses it as a catalyst to produce a synthetic rubber.

TABLE 3-6. CONSUMPTION OF SOLVENTS AS PACKAGING BLEND FOR ALUMINUM ALKYLS (TOTAL U.S. & CANADIAN MARKET)
(AAI and Industry Estimates, 1978)

Solvent	MM lbs./yr
Hexane	5.0
Xylene	1.2
Benzene	2.3
Heptane	0.5
Toluene	1.8
Isopars (n-octane)	0.3 - 0.5
Cyclohexane	*

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*Just entering the market as a replacement for benzene.

An estimated 2.3 million pounds of benzene (312,000 gallons) are shipped annually as an 80-85 wt.% blend of benzene with aluminum alkyl (15 to 20 wt.%). The benzene value of this blend is approximately $235,000.

3.2.1.2 Losses and Environmental Management

In the process of blending aluminum alkyls with solvent (benzene), approximately 2.4% of the benzene (about 55,000 lbs.) is lost as liquid waste and disposed of by incineration. About 0.1% (or 2,000 lbs.) of the solvent is lost to the atmosphere. Atmospheric losses are minimized by handling benzene in closed, nitrogen blanketed tanks and interconnected vent piping systems. Transfer lines are blown free of liquid before they are opened.

The user of the benzene/aluminum alkyl blend purchases an additional 300,000 gal/year (or 2.2 million lbs.) of benzene in tank-wagons to further dilute the catalyst, and for use as a make-up solvent for the polymerization reaction. The approximately 4.5 million lbs. of benzene consumed in this process is vented to the atmosphere in the drying of the polymer crumb. The vented benzene has an estimated value of $458,186.

3.2.1.3 Alternate Solvents

Alternate solvents that are currently used as a protective diluent include cyclohexane, toluene or heptane. The current user of aluminum alkyls dissolved in benzene is phasing in cyclohexane as a substitute, as a result of the impending OSHA regulations for benzene.

3.2.2 Ethyl Cellulose Resins

Ethyl cellulose resins are produced domestically by Dow Chemical Co. and Hercules Corp. These resins, which are soluble in alcohol and aromatic hydrocarbons, are tough, flexible and alkali resistant, and are used in a variety of lacquer coating applications.

One company uses toluene as the process solvent, consuming about 30,000 gallons/year. Until about one and a half years ago, they had used benzene, but switched to toluene due to increasing concern over health and environmental hazards. The other company uses ethanol and diethyl ether as solvents, and has never used aromatic solvents.

Both companies recover and recycle the solvents. Reaction vessels are vented through cooling systems to condense any organics.

3.2.3 Alcohols

Benzene has two main uses in the manufacture of aliphatic alcohols. It is an approved denaturant for ethyl alcohol, under regulations of the Department of the Treasury, Bureau of Alcohol, Tobacco and Firearms (Code of Federal Regulations, 1977). It is also used as an azeotropic agent in the dehydration of 95% ethanol and 91% isopropanol to produce anhydrous alcohols. Higher alcohols (C-4 and above) do not require the use of azeotroping agents for dehydration since they are immiscible with water.

Various government agencies report statistics on domestic production and consumption of ethanol (U.S. Department of the Treasury, 1976; U.S. International Trade Commission, 1977), but do not break out figures for anhydrous alcohol. Table 3-7 shows relevant data for ethanol for 1976, based on government statistics as reported by industry, and on estimates made by two major producers of anhydrous and denatured alcohol. From this it can be seen that about one-third of the annual ethanol production of approximately 300 million gallons is converted to the anhydrous form, using various azeotroping solvents. It should be noted that all data have been converted from pounds and proof gallons to U.S. or "wine" gallons.* The variation in figures is due to the fact that the Bureau of Alcohol, Tobacco and Firearms reports on a fiscal yearly basis.

3.2.3.1 Denatured Ethyl Alcohol

There are three approved formulae for denatured alcohol using benzene (Code of Federal Regulations, 1977). The formulae and their end uses are given in Table 3-8. There is presently no alcohol denatured according to Formula 2-C. Production volumes of benzene-denatured alcohol and the equivalent benzene used for 1976 are shown in Table 3-9.

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*1 wine gallon = 1 U.S. gallon

TABLE 3-7. ANNUAL DOMESTIC PRODUCTION OF ETHANOL, 1976
(millions of gallons)

	Company A (estimate)	Company B (estimate)	Bureau of Alcohol, Tobacco & Firearms	USITC
Anhydrous	110	105		
Denatured (all formulae)		210	220[1]	
Synthetic ethanol, total (190+ proof)	200		189-199[3]	225[2]
Ethanol from fermentation			78-81[3]	(78-81)[3]
Denatured with benzene			25	
Total (anhydrous plus natural and synthetic 190+ proof ethanol)	310		280	305
Imports			9[4]	

[1] U.S. Department of the Treasury, Bureau of Alcohol, Tobacco and Firearms (1976), Summary Statistics, 34.

[2] U.S. International Trade Commission (1977), "Synthetic Organic Chemicals: United States Production and Sales, 1976," U.S. International Trade Commission Pub. 833, Government Printing Office, Washington, D.C.

[3] U.S. Department of the Treasury, Bureau of Alcohol (1976), Summary Statistics, p. 22.

[4] U.S. Department of the Treasury, Bureau of Alcohol (1976), Summary Statistics, p. 23.

TABLE 3-8. DENATURANT FORMULAE AND AUTHORIZED USES AS A SOLVENT

(Code of Federal Regulations, 1977)

Formula 2-B (0.5 gal benzene/100 gal alcohol)	Formula 2-C (0.5 gal benzene/100 gal alcohol plus 33 lbs. metallic sodium)	Formula 12-A (5 gal benzene/100 gal alcohol)
Cellulose plastics. Non-cellulose plastics, including resins. Photographic film and emulsions. Transparent sheeting. Explosives. Cellulose compounds (dehydration). Sodium hydrosulfite (dehydration). Other dehydration products. Petroleum products. Processing pectin. Processing other food products. Processing crude drugs. Processing glandular products, vitamins, hormones and yeasts. Processing antibiotics and vaccines. Processing medicinal chemicals, including alkaloids. Miscellaneous drug processing (including manufacture of pills). Processing dyes and intermediates. Processing perfume materials and fixatives. Processing photographic chemicals. Processing other chemicals. Processing miscellaneous products.	Processing medicinal chemicals (including alkaloids). Processing other chemicals. Processing miscellaneous products.	Cellulose plastics. Non-cellulose plastics, including resins. Adhesives and binders. Processing glandular products, vitamins, hormones and yeasts. Processing antibiotics and vaccines. Processing medicinal chemicals (including alkaloids). Processing blood and blood products. Processing dyes and intermediates. Processing perfume materials and fixatives. Processing rosin. Processing other chemicals. Processing miscellaneous products. Sterilizing and preserving solutions.

TABLE 3-9. VOLUME OF ETHANOL DENATURED WITH BENZENE AND EQUIVALENT BENZENE CONSUMED

(U.S. Dept. of Treasury, 1976)

FORMULA	ALCOHOL (GALLONS)	EQUIVALENT BENZENE CONSUMED (GALLONS)
2-B	24,896,888	124,500
12-A	94,940	4,750
Total	24,991,828	129,250

It can be seen from Department of the Treasury figures that approximately 129,000 gallons of benzene valued at about $100,000 were consumed in 1976 in the denaturing of alcohol. This is in rough agreement with the figures reported by individual companies for pre-OSHA regulation use (i.e., prior to the OSHA Emergency Benzene Standard of May 27, 1977) in Table 3-10, column one. Of the eight alcohol producers who had denatured alcohol with benzene, only one was still using benzene, and total usage as a denaturant had dropped to about 2,000 gallons or less per year. That company anticipates its few remaining customers who use benzene as a denaturant will likely accept a substitute within the next year. The existing customer's end use of the alcohol is at a dilution such that the presence of the original denaturing benzene is in the part per million range, and thus for him, not a health concern. However, the one remaining company who plans to fill customer orders for benzene-denatured alcohol purchases it for this purpose in drums. It is increasingly difficult to find solvent distributors willing to drum benzene (see Section II) and this may be the determining factor in eliminating benzene as an alcohol denaturant.

Benzene loss to the atmosphere occurs when the drums are opened, and during the blending process. This is done either in the open, or with ventilation to the atmosphere. None of the former users reported any environmental controls

TABLE 3-10. BENZENE CONSUMPTION IN THE ETHYL ALCOHOL INDUSTRY

	Denatured, gallons		Anhydrous, gallons		Total, gallons	
	pre-OSHA	post-OSHA	pre-OSHA	post-OSHA	pre-OSHA	post-OSHA
A	10-12,000	-	8-10,000	-	20,000	-
B	4,000	2,000	30-35,000	30-35,000	34-39,000	32-37,000
C	*	-	N.A.[+]	N.A.	-	-
D	*	-	N.A.	N.A.	-	-
E	200	-	N.A.	N.A.	200	-
F	100	-	N.A.	N.A.	100	-
G	*	-	N.A.	N.A.	-	-
H	100	-	N.A.	N.A.	100	-
I	*	-	N.A.	N.A.	-	-
J	3-5,000	-	*	-	3-5,000	-
K	100,000	-	20,000	20,000	120,000	20,000
L	5-10,000	-	YES	-		
M	1,300-2,000	-	*	-		
TOTAL	124-127,000	2,000	58-65,000**	50-55,000	approx. 200,000	approx. 55,000

*Benzene never used in the process, or not used within the last several years.

**Total estimate low since Company L would not supply actual figures.

[+] Those companies for which data is not applicable never produced anhydrous alcohol.

for their denaturing operations. Losses to the atmosphere were estimated at no more than 0.0025% (Sittenfield, 1978), or about 320 gallons of benzene in 1976. Minimal losses of benzene in water, disposed to chemical sewers, were also reported.

The chief alternate solvent being used as a denaturant is toluene. The Bureau of Alcohol, Tobacco and Firearms (U.S. Department of Treasury, 1978) recently issued guidelines concerning authorized use of toluene and rubber hydrocarbon solvent in lieu of benzene. Alcohol denaturers have reported the use of methyl isobutylketone, methanol, gasoline and ethyl acetate as substitutes.

In summary, the pending OSHA standards concerning exposure to benzene in the workplace have had the effect of reducing benzene consumption from about 129,000 gallon/year to less than 2,000 gallon/year, and it is expected to drop to zero once the standard is upheld.

3.2.3.2 Anhydrous Ethyl Alcohol

Benzene has been the chief solvent used in the azeotropic distillation of 95% ethanol to make absolute or anhydrous ethanol. It forms a ternary azeotrope, which carries over the water, leaving behind anhydrous alcohol. The proportions of the three components in the distillate, which boils at 64.6°, are shown in Table 3-11.

TABLE 3-11. AZEOTROPIC DATA FOR ETHYL ALCOHOL
(Advances in Chemistry Series 116, 1973)

A-Component	B-Component	C-Component	B.P. °C	WT. %A	WT. %B	WT. %C
Water	Ethyl Alcohol	Benzene	64.9	7.4	18.5	74.1
Water	Ethyl Alcohol	Cyclohexane	62.6	4.8	19.7	75.5
Water	Ethyl Alcohol	Isopropyl Ether	61.0	4.0	6.5	89.5
Water	Ethyl Alcohol	Toluene	74.4	12	37	51
Water	Ethyl Alcohol	Heptane	68.8	6.1	33.0	60.9

This table also shows the proportions of water carried over using other solvents as azeotroping agents. It can be seen that benzene offers many advantages in terms of boiling point, proportion of water, benzene and ethanol.

The companies which currently produce anhydrous ethyl alcohol are listed in Table 3-12. While all of these companies used benzene as the azeotrope prior to May 1977, only two are continuing to do so. The total quantity of benzene currently used as an azeotrope for anhydrous alcohol is about 50,000 gallon/year, for a value of about $38,000 (see Table 3-10).

TABLE 3-12. PRODUCERS OF ANHYDROUS ETHYL ALCOHOL
(Chemical Week Buyers' Guide, 1977)

IMC Chemical Group, Inc.
Publicker Industries, Inc.
Shell Chemical Co.
Union Carbide Corp.

Companies were generally reluctant to discuss losses. They all operate closed systems, but report pumps, valves, and equipment vents as possible sources of loss to the air. Some liquid loss occurs in the water distilled over, and in side streams containing process impurities. The current overall loss of benzene due to anhydrous alcohol production (equivalent to the make-up purchases) is 50,000 gallon/year or about 200 gallons/day of plant operation.

All companies planning to continue using benzene are aware of the hazards, and anticipate using more stringent controls. These will include flushing hoses before breaking connections when charging benzene, condensers or absorbers on vents, and incineration of liquid wastes rather than chemical sewer disposal.

There are alternate processes for the production of anhydrous ethanol such as countercurrent extraction with a third component, for example, glycerine or ethylene glycol. The added component depresses the vapor pressure of water allowing anhydrous alcohol to be distilled from the top of the extraction column (Lowenheim and Moran, 1976). Industry sources also report the development of a new direct hydration process for making anhydrous ethanol. At least one major company is considering this as an alternate process to benzene extraction.

Some of the companies contacted feel that for their process, there can be no substitute solvent. Those companies that have changed solvents are using cyclohexane. One indicated that they anticipated some process adjustments due to the changeover.

3.2.3.3 Other Alcohols

There are currently four companies that produce anhydrous isopropanol, as listed in Table 3-13.

TABLE 3-13. MANUFACTURERS OF ANHYDROUS ISOPROPYL ALCOHOL
(Lowenheim and Moran, 1975; Industry Sources, 1978)

Company	Plant Site
Atlantic Richfield Co.	Channelview, TX
Exxon Chemical Co.	Baton Rouge, LA
Shell Chemical Co.	Deer Park, TX Dominguez, CA
Union Carbide Corp.	Texas City, TX Whiting, IN

Of these four companies, only two companies had used benzene for the dehydration of isopropanol. One had ceased using it in July, 1977, due to the OSHA Emergency Benzene Standard. Up to this point, they had consumed about 215,000 gallons annually, of which approximately 20,000 gallons was vented to the atmosphere from process losses, and about 196,000 gallons was lost with a side stream purge and incinerated.

The second company was still using benzene (as of the writing of this report) with an annual consumption (and loss) of about 40,000 gallons. This represents about 0.09% of the volume in process. However, they are trying to substitute cyclohexane in their process. Again, assuming about 90% loss through liquid slop which is incinerated or sent to refining operations, and a 10% loss to the atmosphere, there are about 36,000 gallons of benzene lost in the liquid stream and about 4,000 gallons vented to the atmosphere. Thus, current annual consumption of benzene in anhydrous isopropanol production is about 255,000 gallons for a value of approximately $191,000. These results are summarized in Table 3-14.

Benzene is used as an azeotrope in the production of one other anhydrous alcohol, propargyl alcohol, which is used mainly as a corrosion inhibitor in the oil industry. Only one company was found to use benzene for this purpose, consuming about 10,000 gallons/year.

The data for benzene consumption for isopropyl and propargyl alcohols are summarized in Table 3-14, which clearly shows the downward trend in benzene use since the proposed OSHA Standard. The benzene usage should be reduced by an additional 40,000 gallons/year when the second isopropyl manufacturer converts to an alternate solvent. Chief alternate solvents are isopropyl ether and cyclohexane.

TABLE 3-14. CONSUMPTION OF BENZENE AS AN AZEOTROPE FOR OTHER ANHYDROUS ALCOHOLS (gallons/year)

Alcohol	Benzene Consumed		Estimated Liquid Losses*		Estimated Atmospheric Losses	
	Pre-OSHA	Post-OSHA	Pre-OSHA	Post-OSHA	Pre-OSHA	Post-OSHA
Isopropyl	215,000	Nil	196,000	Nil	20,000	Nil
Isopropyl	40,000	40,000	36,000	36,000	4,000	4,000
Propargyl	10,000	10,000	9,000	9,000	1,000	1,000
TOTAL	265,000	50,000	241,000	45,000	25,000	5,000

* Incinerated or fuel blended

3.2.4 Bisphenol-A

Bisphenol-A is made by reacting phenol with acetone in the presence of an acid catalyst. The four manufacturers are listed in Table 3-15.

TABLE 3-15. MANUFACTURERS OF BISPHENOL-A
(Chemical Marketing Reporter, 1977)

Company	Plant Site
Dow Chemical U.S.A	Freeport, TX
General Electric Co.	Mount Vernon, IN
Shell Chemical Co.	Houston, TX
Union Carbide Corp.*	Penuelas, PR

* Ceased production at Marietta, OH plant

The basic process produces crystalline Bisphenol-A in a slurry with phenol. The major producers have made various refinements on the synthesis and purification process, whereby the water and phenol are removed in order to meet the demand for higher quality for use in polycarbonate resins. Polycarbonates now occupy 40% of the Bisphenol-A market, and epoxy resins 47%. Total consumption of Bisphenol-A in 1977 was 460 million pounds (Chemical Marketing Reporter, 1977).

Only one producer has ever used benzene in the extraction process, and they ceased doing so in mid-1976. The substitution of an alternate solvent was the result of an internal process change, and not due to pending OSHA regulations. In 1975, the last full year of benzene use, 20 million pounds or 2.99 million gallons of benzene were consumed. This company has substituted methylene chloride as the solvent.

3.3 FORMULATED INDUSTRIAL AND CONSUMER PRODUCTS

Solvents are used in the manufacture of many formulated products. Among the products which may require solvents are:

- Adhesives and rubber based cements
- Paints, coatings and allied products
- Dry cleaning agents
- Degreasing agents
- Furniture and floor polishes
- Printing inks

There are many different solvents used to formulate industrial and consumer products. The more common ones include:

- Aliphatic
  - Hexane
  - Heptane
  - Mineral spirits
- Aromatic
  - Benzene
  - Toluene
  - Xylene
- Ketones
- Chlorinated solvents
- Alcohols

Historically, benzene as an active solvent has been associated with the formulation of adhesives and rubber based cements, tire repair kits, tire manufacture, paints and allied products, and gravure printing inks. The use of benzene in gravure printing ink manufacture or in gravure printing processes has been eliminated (U.S. Department of Labor, OSHA, 1977; Industry Sources, 1977). Consequently, no detailed investigation of this former use was made for this study.

The next two sections (3.4 and 3.5) will be devoted to a review of potential uses of benzene as a solvent in the formulation of adhesives and rubber-based cements, tire repair kits, tire manufacture and paints and allied products.

3.4 FORMULATED PRODUCTS: ADHESIVES

The adhesives industry as a whole is dominated by companies with fewer than 20 employees. According to the 1972 Census of Manufactures the total number of establishments in SIC 2891 was 463. Those with 75% or more product specialization accounted for 422 establishments. Of these 187 or 39% had 20 or more employees. The specific segment of interest, SIC 28914, Synthetic Resins and Rubber Adhesives, had 252 establishments, 171 of which had 75% or more product specialization.

The adhesives industry produces a wide diversity of products based on the type of adhesive substance used. The types of adhesives, the form in which they are used, the method of use and applications are given in Table 3-16. Table 3-17 classifies adhesives based on the origin of the principal components, and Table 3-18 classifies adhesive systems.

TABLE 3-18. CLASSIFICATION OF ADHESIVES BY PHYSICAL TYPE
(M. Sittenfield & Associates, 1978)

- Solvent Responsive
  - aqueous solution
  - solvent solution
  - emulsion type
  - remoistenable
- Chemically Reactive (Thermo-setting)
- Pressure Sensitive*
- Hot Melt

* Pressure sensitive adhesives are applied to a backing from a solvent solution.

Solvents used to formulate solvent type adhesives can include benzene, toluene, xylene, hexane, heptane, mineral spirits, ketones, and alcohols.

TABLE 3-16. BASIC TYPES OF ADHESIVES AND APPLICATIONS

(M. Sittenfield & Associates, 1978)

Main Ingredient	Physical Characteristics	Form Used	Method of Use	Maximum Useful Temp. °C	Bonding Applications
Acrylics	Thermoplastic	Solution, Emulsion, Polymer-Mon. Mixt.	Cured by heat, U.V. Radiation, Catalysts	50	Pressure Sensitive Tapes, (VAC copolymers) paper & packaging, acrylic plastics, glass, metals, leather, and textiles
Allyls (Unsaturated Polyesters)	Thermosetting	Alone	Heat cured with Benzoyl Peroxide Catalyst		Optical Cement
Cellulose Derivatives					
(A) Acetate	Thermoplastic	Solution With Plasticizers	Solvent Evaporation	Ca50	Household Cements, balsa wood (model aircraft), cellulose acetate plastics, Photographic film
(B) Acetate-Butyrate	Thermoplastic	Solution with Plasticizers	Solvent Evaporation	>50	Balsa wood (Model aircraft), Cellulose Acetate Plastics, Photographic film
(C) Caprate	Thermoplastic	Solution with Plasticizers	Solvent Evaporation	70	Optical Cement
(D) Nitrate	Thermoplastic	Solution with Plasticizers	Solvent Evaporation	Depends on composition	Household cement for glass, leather fabrics, paper, metals, wood, plastics
Chlorinated Polyethers	Thermoplastic	Alone	Heat Seal	125°	Plastics (e.g. Polyvinyl chloride), hot water equipment, valves, etc.
Coumarone-Indenes, Petroleum Resins and Polyterpenes	Thermoplastic	Alone or in Solution with Aromatic Solvent	Solvent Evaporation or pressure sensitive applications		Modifier for Polystyrene, rubber adhesives, rubber, pressure sensitive tapes
Cyanoacrylate	Cold Setting	Alone	Polymerizes at R.T.	80-100	Wood, glass, metals, rubbers, plastics, cork felt, leather
(A) Epoxy	Thermosetting	Alone (Catalyst added just prior to use)	Heat cured with Anhydride or Amine Catalyst	95	Structural adehsives for metals, glass, ceramics, wood, rubbers, plastics
(B) Epoxy-Phenolic	Thermosetting		High temp. cured	>260	High temp. Structural applications - missiles, jets, etc.
(C) Epoxy-Resorcinol	Thermosetting		High Temp. cured	>260	High Temp. structural applications - missiles, jets, etc.
(D) Epoxy-Polyamide	Thermosetting		Heat cured	90	Metals, glass, ceramics, rubbers, wood, leather, plastics
Furanes	Thermosetting	Alone	Low Temp. cured using acid catalyst	150	Modify other resins, chemically resistant cements, phenolic laminates, Gap filling

TABLE 3-16. BASIC TYPES OF ADHESIVES AND APPLICATIONS (continued)

Main Ingredient	Physical Characteristics	Form Used	Method of Use	Maximum Useful Temp. °C	Bonding Application
(Socyanates Polyurethanes)	Thermosetting	In Solution	Heat cured		Metals, rubbers, glass plastics, fabrics, leather, modifier and curing agent for rubber-based adhesives
Melamine-Formaldehyde	Thermosetting	Solution or Paste	Heat cured with catalyst	90	Plywood, furniture, modifier urea adhesives
Nylon (Polyamide)	Thermoplastic	Alone or in Solution	Heat seal or solvent evaporation	Low	Epoxy modifier, paper, metal foil, leather plastics, cellophane, packaging labeling
Pehnolic					
(A) Phenol-Formaldehyde	Thermosetting	Alone in film, liquid or powder form	Cured by heat and pressure	100	Plywood, reinforced plastic laminates (Phenolics, ureas, melamines), metal to wood
(B) Phenolic-Epoxy	Thermosetting	Alone	High temp. cured	>260	High temp. structural applications - missiles, jets, etc.
(C) Phenolic-Neoprene	Thermosetting	Alone in film, liquid	Heat cured	93	Metals, rubbers, many plastics, wood, glass ceramics - may be modified by isocyanates
(D) Phenolic-Nitrile	Thermosetting	Alone	Heat cured under pressure	150-270	Structural metals, brake shoes, linings, rubbers, plastics, wood, glass, ceramics
(E) Phenolic-Polyamide	Thermosetting	Phenolic resins and polyamide film applied separately	Heat and pressure cured	>150	Metals for high temperature applications - e.g. aircraft structures
(F) Phenolic-Vinyl (e.g. polyvinyl Butyral)	Thermosetting and thermoplastic mixture	Apply liquid phenolic, then dust polyvinyl formal powder	Heat cured under pressure	85	Structural metals, cyclized rubber, metals, and plastics, gap filling, metal to wood, (Phenol used to lower cost of resorcinol adhesive)
(G) Phenolic-Resorcinol	Thermosetting	Alone as liquid	Cold setting or hot pressed	180	Modifications of phenolics, wood, plastics, gap filling metal to wood, (Phenol used to lower cost of resorcinol adhesive)
Polyesters (Alkyds) and unsaturated Polyesters	Thermosetting and Thermoplastic	Alone	Cured by heat or catalyst	150	Fiberglass laminates optical cements, modifiers for isocyanates
Protein					
(A) Animal & Fish		Hot water Solution	Solvent Responsive	60	Bookbinding, abrasives, wood, leather, cloth,
(B) Casein		Water Solution	Cold Press	60	Wood, Paper coating, construction, packaging, leather, cloth

TABLE 3-16. BASIC TYPES OF ADHESIVES AND APPLICATIONS (continued)

Main Ingredient	Physical Characteristics	Form Used	Method of Use	Maximum Useful Temp. °C	Bond Application
(C) Soy Bean		Water Solution	Solvent Responsive	60	Low-Grade plywood, paper lamination, wallpaper coating
(D) Zein		Alone	Used in Hot Melt Formulation		Wood, paper, cloth and glass
Resorcinol					
(A) Resorcinol-Formaldehyde	Thermosetting	Alone as liquid	Cold setting or hot pressed	180	Structural applications (boats, roof trusses laminated timber) modification of phenolics, wood, plastics, gap filing metal to wood
(B) Resorcinol-Phenolic	Thermosetting	Alone as liquid	Cold setting or Hot pressed	180	Wood, plastics, gap filling, metal to wood (phenol used to lower cost of resorcinol adhesive)
Rubber	Thermoplastic & Thermosetting				
(A) Natural		Solution or Latex	Set by solvent Evaporation and/or vulcanization	Unvulc. 65° Vulcanized 95°	Pressure sensitive applications, bootwear, leather, rubber, paper, felt, textiles, metal foil to paper or wood, sponge rubber, also a modifier for phenolics and epoxies in structural, automotive and aircraft use.
(B) Synthetic (e.g. Neoprene, SBR)		Solution or Latex		90-150	
(C) Reclaimed (Natural & Synthetic)		Solution or Emulsion			Non-Structural applications, e.g. paper, cloth and rubber
Silicate	Thermosetting	Aqueous Solution	Sets by loss of water	>250	Corrugated paperboard, glass, stone paper to aluminum foil, low grade plywood, heat insulating products (asbestos, mica, etc.)
Silicones	Thermosetting	Solution	Room temperature and heat cure	>250	Pressure sensitive tapes, insulating tapes, silicone rubber, high temp. structural adhesives, (e.g. blended with epoxies)

TABLE 3-16. BASIC TYPES OF ADHESIVES AND APPLICATIONS (continued)

Main Ingredient	Physical Characteristics	Form Used	Method of Use	Maximum Useful Temp. °C	Bond Applications
Starch & Dextrins	Thermosetting	Aqueous Solution	Water Responsive	CA. 100	Packaging, paper converting, labeling
Styrene (Butadiene Copolymer-GRS)	Thermosetting	Solution	Solvent Evaporation	70-95	General Purpose (see synthetic rubbers)
Urea-Formaldehyde	Thermosetting	Syrup or Powder	Hot and cold setting	60	Furniture, plywood, corrugated fiberboard, some plastics (phenolics, ureas, melamines)
Vinyls					
(A) Polyvinyl Acetals	Thermoplastic	Solution	Evaporation or solvent		Phenolic modifier in structural metals, safety glass
(B) Polyvinyl Acetate	Thermoplastic	Water emulsions, solvent solutions, hot melts, powder	Cold setting	50	Food packaging, wood, paper, paper, leather, cloth, metals, glass, ceramics, many plastics, bookbinding
(C) Polyvinyl Alcohol	Thermoplastic	Water Solution	Evaporation of Water	65	Food Packaging
(D) Polyvinyl Chloride	Thermoplastic	Solution in chlorinated solvent	Evaporation of solvent		Used as copolymer with PVAc for bonding vinyl plastics to metals and glass; also used with synthetic rubber
Waxes	Thermoplastic	Alone	Hot Melt	Low	Compounded with elastomerics for added flexibility, temporary bonds for metals, glass, labels, packaging

TABLE 3-17. CLASSIFICATION OF ADHESIVES BASED ON ORIGIN OF THE PRINCIPAL COMPONENTS

(M. Sittenfield & Associates, 1978)

Component Origin	Natural Adhesives
Animal	Animal hide or bones; fish; casein (derived from milk); blood albumin
Vegetable	Starch and dextrin; soybean
Natural Resins	Bitumens (including asphalts); coumarone-indene; petroleum resins; polyterpenes; shellac; resins; gum arabic
Inorganic	Silicates; ceramic compositions
Elastomeric	Natural rubber (and its derivatives); chlorinated rubber, cyclized rubber; rubber hydrochloride
	Synthetic Adhesives
Elastomeric	Synthetic rubbers (neoprene, nitrile, polysulfide, SBR, silicone); reclaimed rubbers
Thermoplastic Resins	Vinyls; cellulosics, acrylics; cyanoacrylates; polyamides, polyisobutylenes; hydrocarbon resins; polystyrenes
Thermosetting Resins	Phenolics; ureas and melamines; epoxides; furanes; resorcinols; polyesters (alkyds); polyurethanes; silicones

Table 3-19 lists the principal polymers used in the formulation of water and solvent based adhesives.

The information summarized in these tables shows the relation of the rubber-based adhesives to the adhesives industry in general, and also shows other segments of the adhesives industry in which solvents are used.

Interviews with adhesive manufacturers indicate that there are no uses of benzene as an active solvent in non-rubber based adhesive formulations. One small company reported that it does use benzene in small quantities (300 to 600 gallons per year) in formulating some epoxy cements. However, this use is atypical for the industry.

3.4.1 General Consumption Patterns

The major end use industries for adhesives in terms of weight and the major adhesive components used are given in Table 3-20.

TABLE 3-20. END USES AND ADHESIVE COMPONENTS
(Marcus Sittenfield & Associates, 1978)

End Use	Estimated % of Total Adhesives Manufactured	Major Adhesive Components
Paper & Packaging	32	Starch, vinyls, silicates, animal, protein, acrylic
Wood Products	25	urea, phenolic, protein
Structural & Metal	33	phenolic, elastomeric, vinyl, epoxy
Miscellaneous		
Industrial Specialties	8	elastomeric, vinyl, acrylic
Household	0.6	vinyl, elastomeric, cellulosic, epoxy, animal

A review of the types of adhesives used in each of these industries shows that solvent based adhesives find three applications: structure and metal, miscellaneous industrial specialties, and household uses.

TABLE 3-19. PRINCIPAL POLYMERS FOR WATER AND SOLVENT BASED ADHESIVES

WATER SOLUTION BASED	WATER (LATEX) OR SOLVENT BASED	SOLVENT BASED
Starch & Dextrin	Rubber (natural and synthetic)	Nitrocellulose
Gums	PVAc and copolymers	Cellulose acetate butyrate
Glue	Polyvinyl chloride and copolymers	Cyclized rubber
Albumin	Polyvinyl ethers	Polyisobutylene
Sodium Silicate	Polyvinylidene chloride & copolymers	Polyurethane
Casein	Polyacrylates and polymethacrylates	
Sodium Carboxymethylcellulose	Polyamides	
Lignin	Asphalt	
Polyvinyl Alcohol	Urea-formaldehyde	
Methyl Vinyl Ether - Maleic Anhydride Copolymer	Phenol-formaldehyde	
Polyvinyl Pyrollidone (PVP)	Resorcinol formaldehyde	
	Rosin esters	

Areas of application in the structural and metals market encompasses the entire range of mechanical industries, including construction of automobiles, aircraft, machinery, steel structures, tanks, railroad equipment, ships, electrical equipment, tools, etc. These end uses can be classified according to their degree of importance as follows: building materials, automotive, tire cord, aircraft and missiles and other metals. The current market for adhesives in these applications is estimated* to be of the order of $500 million per year. Solvent-based adhesives find limited use in these applications. They are generally required for such uses as joining plastic or plastic coated metals, plastic pipe and other plastic building materials. Benzene is not used to formulate the solvent-based adhesives used for structural and metal applications. Most of the adhesives used in the automotive and the tire tread industries are solvent formulated rubber adhesives and will be discussed in Section 3.4.2.1.

The category of miscellaneous industrial specialties includes a multitude of adhesive applications, the most important of which are pressure sensitive products, non-woven fabrics, shoes, and coated and bonded abrasives.

Pressure sensitive adhesives are manufactured by applying the adhesive to the backing by solvent coating, calendering or aerosol spraying. The solvent is removed (and recovered) during the manufacture of the pressure sensitive material. None of the solvent reaches the consumer. The adhesives used in pressure sensitive formulations comprise styrene-butadiene rubber, nitrile, and other rubber types. Acrylics, silicones and similar materials are also used. Benzene is not a component of the solvent blends used in the manufacture of pressure sensitive tapes. However, it may be an accidential contaminant of some of the solvents used, such as toluene, hexane, or mineral spirits. Pressure sensitive products represent the largest market share of the miscellaneous products market.

Adhesives for the non-woven fabric market are either hot-melt or water based latex adhesives. Solvent formulated adhesives are not used.

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* Industry sources

Elastomeric rubber-based and polyurethane adhesives are those most commonly used in shoe and footwear production. Industry information indicates that over 90% of the elastomeric materials are used as solvent cements, the remainder in latex form. This market will be discussed further in Section 3.4.2.

No solvent-based adhesives are used in the manufacture of coated and bonded abrasives.

Household adhesives form a relatively small market, accounting for less than 1% of the total adhesives sold and produced in the United States. The estimated share of the household market held by each of the adhesive types is given in Table 3-21. The rubber "contact cements", the cellulosics and other plastic cements formulated with solvents share an equal part of the household adhesive market, which is dominated by the polyvinyl acetate water emulsion adhesives. None of the solvents used for the cellulosics or other plastic cements use benzene as a component of the blend.

TABLE 3-21. ESTIMATED SHARE OF HOUSEHOLD ADHESIVE MARKET
(M. Sittenfield & Associates, 1978)

Polyvinyl Acetate	49.0%
Rubber "contact cements"	14.5
Cellulosics and other plastics	14.5
Animal and fish	9.1
Epoxy	3.6
All others	9.0

Rubber "contact cements" and other elastomeric adhesives will be discussed in greater detail in Section 3.4.2.

3.4.2 Solvent Type Rubber-Based Adhesives

Solvents are used in the manufacture of most rubber-based adhesives and as an adjunct in the manufacture of rubber products in order to promote bonding. Rubber-based adhesives are used chiefly for industrial applications, with no more than six percent of the total manufactured used in the home or office. The estimated percent consumption of rubber adhesives by end use is shown for 1978 in Table 3-22.

TABLE 3-22. END USE CONSUMPTION OF RUBBER-BASED ADHESIVES
(M. Sittenfield & Associates, 1978)

Rubber Industry	
Tires	57.6%
Industrial rubber products	0 %
Reclaimed rubber	0 %
Tire and tube repair patch kits	2.0%
Automotive	20.5%
Shoe manufacture and repair	16.4%
Household	3.5%

3.4.2.1 Tires and Tubes

Elastomeric solvent-based adhesives and solvents are used in the manufacture of tires to cement the plies during the build-up of the tire prior to molding and vulcanizing. Solvents are also used directly to "freshen" the rubber when it is dry and has lost its tackiness.

Modern tire manufacturing techniques do not require cement or solvent tackifers. This is a result of changes in rubber formulations that provide the rubber with sufficient tack so that adhesives do not have to be used in order that the plies bond together during the build-up process. When additional tack is required, some of the manufacturers contacted indicated they used phenolic resins or water-based rubber cements.

Another change which is reducing the use of elastomeric solvent-type adhesives and solvents by the tire industry is the increasing popularity of radial tires, whose manufacture requires little if any rubber cement.

The amount of rubber cement used in the manufacture of tires is estimated* to be of the order of 140 million pounds for 1977. On the basis that solvents represent about 80% by weight of rubber cements, the solvent consumption in this application is about 15 million gallons. As noted, solvents are also used occasionally during the manufacturing to rewet or tackify rubber plies that have lost tack. The volume required for this use is estimated not to exceed 20% of the quantity used in the adhesives, or about 3 million gallons.

Based on interviews with six of the major tire manufacturers, the total solvent use for this industry in 1977 was estimated to be between 20 and 25 million gallons.

Solvents used to formulate rubber adhesives are known variously as "Rubber Maker's Naphtha" or "Rubber Solvent". They are special fractions of aliphatic hydrocarbons ranging from hexane to octane. Since the issuance of the proposed OSHA benzene regulations, the tire manufacturers are requiring that their suppliers provide the solvents with a maximum benzene content of 0.5%.

There is considerable doubt on the part of producers that the benzene content can be reduced below the 0.5% level without the expenditure of significant sums by refiners, and a consequent substantial price rise which could prove prohibitive to many manufacturers whose products require solvents.

All the solvent used in tire manufacturing industry applications is vaporized and lost into the atmosphere. The probable benzene loss, at 0.5% concentration in the solvents used, is calculated to be between 100,000 and 125,000 gallons annually. This volume is dispersed from over 200 establishments (Census of Manufacturers, 1972) scattered throughout the United States. The volume of benzene lost per year per establishment is calculated to be between 500 and 625 gallons.

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*Industry estimates and Marcus Sittenfield & Associates calculations.

3.4.2.2 Tire Retreading

Rubber adhesives and solvents are used in the manufacture of retread tires to develop tack in the old rubber and allow new tread stock to adhere to the tire carcass prior to revulcanization. According to an industry spokesman, about six grams of solvent are used per kilogram of new rubber (about 0.1 ounces (wt.) per pound). The average amount of rubber used is 10 pounds per passenger tire and 35 pounds per truck tire.

Trade sources (Modern Tire Dealer, 1978) indicate about 13 million truck tires, 32 million passenger tires, and 14.5 million snow tires were retreaded in 1977. The calculated solvent consumption in tire retreading is shown in Table 3-23.

TABLE 3-23. CALCULATED SOLVENT CONSUMPTION FOR RETREADING, 1977

Tire type	Millions of Tires	Solvent used, MM lbs.	MM gals.
Passenger-replacement	32	4.23	0.55
-snow	14.5	1.92	0.25
Truck-replacement	13	6.01	0.78
Total		12.16	1.58

All of this solvent is lost to the atmosphere during retread processes. The solvents used in tire retreading are petroleum naphthas; no benzene is used in the solvent formulation except as an accidental contaminant of the naphthas. As with the tire manufacture industry, the solvent is being purchased based on supplier's ability to reduce the benzene content to or below 0.5%.

On this basis, the potential benzene loss in the U.S. from tire retread operations is calculated to be 7,500 gallons per year at dispersed locations.

3.4.2.3 Industrial Rubber Products

Industrial rubber products cover a wide range of articles manufactured by molding or laminating processes. These include hoses, seals, belts, rolls, life rafts, and industrial tires. None of the companies contacted used solvents in the manufacture of this class of products. No benzene is used, or has been used, in manufacturing processes for this segment of the rubber industry.

3.4.2.4 Rubber Reclaiming

Scrap rubber and scrap tires are reclaimed by the use of one of two processes. One employs mechanical grinding methods; the other is treatment with sodium hydroxide. Neither process uses a solvent. Large quantities of reclaimed rubber are used in the manufacture of rubber cements, chiefly because it is cheaper than virgin synthetic or natural rubber.

Some petroleum (naphtha) solvents may be used for cleaning process equipment. However, none of the companies contacted reported the use of benzene.

3.4.2.5 Tire and Tube Repair or Patch Kits

Tire repair kits are largely sold to tire repair shops, garages and service stations. They are also used to a limited extent by consumers to repair bicycle and automobile tires. There are no published statistics available to indicate the size of the industry or categorize the type of businesses. However, according to industry sources, there are about 40 manufacturers, and five who share the bulk of the business. They are shown in Table 3-24.

TABLE 3-24. MAJOR TIRE REPAIR KIT MANUFACTURERS

	no. of employees
Egan Manufacturing Co.	*
Patch Rubber	20-49
Technical Rubber Co.	100-499
Kex Rubber Co.	50-99
Better Monkey Grip Co.	100-499

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*Not available.

Benzene is no longer used by the industry in the solvent adhesive package that is included in the tire repair kit. Only one company stopped using it as a direct result of the proposed OSHA regulations. Most companies had switched solvents earlier because of benzene's known toxicity. The alternate solvents reported used are petroleum naphthas and aromatics such as toluene, which contain less than 1% benzene. The total volume of solvent used in tire repair kits was estimated by one company to be of the order of 100,000 gallons per year.

Environmental losses of solvents used in tire repair kits are substantially 100% to the atmosphere. Considering a maximum content of 1% benzene (as an accidental contaminant), the probable maximum exposure of the environment to benzene from this source is 1,000 gallons per year. This volume is lost in very small quantities at multiple sites.

3.4.2.6 Miscellaneous Uses

Elastomeric adhesives find use in many phases of shoe and footwear production either as a structural (permanent) or non-structural (temporary holding) adhesive. The major operations requiring adhesives are:

(1) Making the shoe upper
(2) Lasting
(3) Sole assembly
(4) Shoe repair

Latex and solvent based elastomers are the adhesives most commonly used in shoe production and shoe repair. Polyurethane and hot melt adhesives are now making inroads into the elastomer market. This is due to a changeover from stitching to bonding of insoles and outsoles, and to increased production line speeds and automation.

Industry reports indicate that adhesive consumption by the shoe manufacturing and repair industry is of the order of 7 million pounds of solids. It has been estimated that 38% of this quantity are rubber and neoprene based adhesives, 43% polyurethane and 19% hot melts.

Over 90% of the elastomeric (rubber, neoprene and polyurethane) materials used are solvent based, the balance are in latex form.

The calculated volume of solvent used in this industry, based on the previously noted percentages, is about 15 million pounds or 2.2 million gallons.

The solvents used in rubber-based cements are usually blends of toluene, toluene-xylene, naphtha, acetone and methyl ethyl ketone. No benzene is used in the solvent formulations. Accidental benzene contamination of these solvents may occur as a result of the petroleum refining process. This contamination is currently being limited to 0.5% to meet the requirements of the proposed OSHA regulations.

3.5 FORMULATED PRODUCTS: PAINTS AND ALLIED PRODUCTS

Paints, paint thinners, and paint removers all use solvents. The solvents used in this industry include petroleum distillates, aromatic chemicals, ketones, chlorinated chemicals and alcohols. "Rule 66" in Los Angeles County* and "Regulation 5"** in the San Francisco area are partially responsible for the elimination of benzene and other photo-oxidizable hydrocarbons from paint formulations. OSHA regulations on permissible solvent concentrations in the workplace together with the California air quality regulations have resulted in the greater use of water based paints which are now used both for interior and exterior applications. Electrostatic coating and other technologies are being used in many industrial applications to eliminate the presence of solvents.

Paint thinners are formulated from turpentine or petroleum naphthas. Benzene is not and has not been an ingredient of this group of products.

3.5.1 Paints and Coatings

Benzene's solvent powers and high volatility made it a desirable component in solvent blends for the manufacture and formulation of nitrocellulose lacquers, cellulose esters, airplane dopes, varnishes and stains. According to benzene manufacturers, and distributors and paint manufacturers+, there has been a move away from benzene in these areas for the past 10 years. It is reported that benzene has been eliminated from the solvent blends used in paint formulations because of known toxic and flammable properties. The paint industry spokesmen also noted that there is a trend away from solvent based paints and coatings toward the use of water-based emulsion type paints. It is estimated that by 1981 only 22% of all paint sales will contain an organic solvent (Chemical Week, 1976).

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*South Coast Air Quality Management District Regulation 442: Usage of Solvents, Reg. 443: Labelling of Solvents.

**Air Pollution Episode Plan, adopted March 21, 1974, revised July 16, 1975.

+Shell, Exxon, Texaco, Gulf Oil, Charter Oil, AMSCO, Glidden, du Pont, Sherwin-Williams.

3.5.2 Paint Removers

Until 1977, the largest solvent use of benzene by the paint and allied products industry had been as a component of low-cost paint removers and strippers. According to industry sources, perhaps one out of 10 paint remover formulations used benzene to the extent of 25 to 50 volume percent of the total solvent. These were usually the low cost brands produced either under the manufacturer's label or packaged as a "private label" brand for sale by paint manufacturers or various store chains.

Benzene-containing paint remover formulations were being produced until the early part of 1977. Since then, the companies contacted stated they have removed benzene as a direct component of their formulation. However, it is possible that some of the older products which contain benzene are still on the shelves of some stores.

Specific data on the amount of benzene that may have been used by companies formulating paint removers in recent years is difficult to obtain because of the reluctance of companies to reveal figures they consider confidential. Industry sources, including benzene manufacturers and distributors, estimated that between 300,000 and 400,000 gallons of benzene may have been used in these products in 1976.

The 1972 Census of Manufactures (U.S. Department of Commerce, Bureau of Census, 1976) reported the quantity of shipments of paint and varnish removers was 12.6 million gallons. Industry spokesmen believe that the total volume of these products has not changed appreciably since then. Industry sources estimate that a maximum one out of ten, or 10% of all paint and varnish remover products produced prior to 1977 contained benzene, with an average benzene content of between 20 and 50%. The maximum 1976 consumption of benzene in paint removers is calculated to be in the range of 300,000 to 600,000 gallons excluding the benzene content resulting from its accidental presence in other solvents. This confirms the industry reported information.

The major companies in the paint remover field report that they have discontinued the manufacture and sale of benzene-containing products as of 1977, probably about the time of the issuance of the regulatory notice by OSHA (Federal Register, 1977). However, one distributor-reseller reported that he had sold a small volume (less than 5,000 gallons) of benzene to a small company manufacturing a furniture refinisher for commercial use (not consumer sales).

The paint and varnish removers on the market today are blends of materials such as acetone, methanol, toluene, xylene, methylene chloride and naphtha-type hydrocarbons. Of these, toluene and the naphthas could be contaminated with a maximum of 1% benzene.

The "Briefing Package and Related Documents Regarding Benzene" (U.S. Consumer Product Safety Commission, 1977) contained letters from the following paint remover manufacturers:

MANUFACTURER	PRODUCTS
United Gilsonite Laboratories	Raizoff Paint and Varnish Remover
Savogran Company	Kutzit Paint and Varnish Removers
Cook Paint and Varnish Co.	Kut-All Paint and Varnish Remover
Elliott Paint and Varnish Remover	Penetrating Oil Stain
Reliable Paste and Chemical Co.	Stay Wet Liquid Remover Comet Liquid Remover Antique Refinishers Remover Stay Put Heavy Bodied Remover Dox Liquid Brush Cleaner

They stated that none of their products currently contain benzene. Either they have removed the specific formulation from their product list or have reformulated the product eliminating benzene as a component.

The large paint companies such as Glidden, Sherwin-Williams and duPont all reported (1977) that they do not use benzene as a solvent in the formulation of any of their products nor do they buy solvent blends where benzene concentration is more than 3%, preferably less than 1%. (These specification limits have been reduced to conform to the OSHA proposed regulations of 1978).

A major paint manufacturer stated that as of May 1977, the only paint remover product they had produced that contained benzene had been formulated. No product currently manufactured contains benzene according to the spokesman. A spokesman for another company reported that benzene had been eliminated from their products.

A spokesman for another coatings manufacturer reported that his company has not used benzene as a solvent or as a component or any of their industrial paints, coatings and related products for a number of years. He stated that the coating and paint industry has recognized benzene to be a major health hazard and voluntarily removed it from their products.

The distributors and resellers of solvents and solvent blends confirmed the statements of the paint remover formulators that benzene is no longer being bought for this use.

One formulator who sells solvent blends for many purposes stated that until 1977, they sold a solvent blend containing benzene to companies making paint removers. As of the middle of 1977, they reformulated their blend eliminating benzene.

The Houston district branch of one of the largest national distributor companies sold an average of 60,000 to 70,000 gallons of benzene per year. About one quarter (15,000 to 17,000 gallons) of this went for chemical intermediate use. About one half (30,000 to 35,000 gallons) was sold to companies formulating paint removers. The balance (15,000 to 17,000 gallons) was sold for miscellaneous industrial solvent uses. A representative of this company stated they no longer sell benzene to any of these markets.

Another benzene distributor in the southwest market area reported that at one time they formulated about 50,000 gallons/year of paint stripper blends containing 20% benzene. Several years ago this product was reformulated to eliminate benzene.

The Texas Air Control Board (1977) provided AAI with the opportunity to review non-confidential data obtained from all paint, rubber and chemical companies in Texas that had shown hydrocarbon emissions in a state wide monitoring effort. Some of the data was obtained in 1972, updated in 1973 to include only companies whose total of all types of chemical emission exceeded 50 tons per year and further revised in 1975 to include selected companies with large air emissions. None of the companies which replied to the questionnaire sent by the Texas Air Control Board reported the use of benzene.

The solvents used to formulate paint removers and strippers are vaporized into the atmosphere during use.

The estimated benzene emission to the atmosphere for 1976 is calculated in Table 3-25.

TABLE 3-25. ESTIMATED ATMOSPHERIC BENZENE LOSSES FROM PAINT REMOVERS, 1976

(M. Sittenfield & Associates, 1978)

Benzene containing formulations	300,000 to 600,000
Accidental contamination*	190,000
Total Loss	490,000 to 790,000

Present benzene losses (1978) to the atmosphere due to the contamination of petroleum hydrocarbon solvents will not exceed 30,000 gallons, based on a maximum content of 0.5% benzene in the solvent.

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* 12,600,000 gallons x 50% hydrocarbon content x 3% benzene = 190,000 gallons

3.6 SUMMARY

Benzene consumption as a solvent has been approximately halved in the two year period from 1976 to 1978. It has been eliminated altogether from the formulated industrial and consumer products (where there was almost 100% loss to the environment). As shown in Table 3-26, consumption has dropped from about 4.8 million gallons in 1976 to an estimated 2.8 million in 1978.

The OSHA Emergency Benzene Standard of May, 1977 is the major factor contributing to the decline in benzene consumption, although some companies reported moving to alternate solvents prior to the OSHA action, based on the known toxicity of benzene and its large increase in price, relative to other solvents.

The trend is definitely towards eliminating benzene solvent consumption wherever feasible. The smaller volume users, for example, those in the pharmaceutical industry, are more inclined to eliminate benzene since they have no uses for it other than as a solvent, and because they are having increasing difficulty in obtaining benzene in small quantities. This is borne out in Tables 3-1 and 3-3, which show the greatest drop in use in this area.

Those who consume benzene as an adjunct in general organic syntheses frequently use benzene in their plants as a chemical intermediate, and are thus more likely to have well developed workplace and pollution control systems, and less need to look to alternate solvents.

TABLE 3-26. SUMMARY OF BENZENE SOLVENT CONSUMPTION

Consumption Area	Estimated Consumption	
	1976	1978
General Organic Synthesis	2,962	2,214
Pharmaceutical Synthesis	650	220
Small Volume Chemicals		
Aluminum Alkyls	312	312
Alcohols	465	100
Bisphenol-A	0	0
Ethylcellulose	0	0
Formulated Industrial & Consumer Products		
Adhesives	0	0
Rubber-based adhesives	0	
Tire manufacture	0	0
Tire retreading	0	0
Industrial rubber products	0	0
Tire patch repair kits	100	0
Miscellaneous		
Automotive	0	0
Shoe	0	0
Paints and Allied Products		
Paints & coatings	0	0
Removers	300 to 500	0
TOTAL	4,789 to 4,989	2,846

SECTION IV. USE ALTERNATE ANALYSIS

Benzene has strong solvent properties for many organic chemicals. Its availability and, until recent years, its relative low cost, has made it the solvent of choice for many uses. However, because of its recognized toxicity, and the promulgation of regulations by OSHA, work has been done to find substitutes that are less hazardous.

The major emphasis in developing alternate solvents has been for formulated products that are used by the general public or by small companies who would find the cost to meet in-plant safety measures excessive.

The chemical and related process industry is a major user of benzene as a solvent adjunct in chemical manufacturing. Benzene has been selected for this use because of its excellent solvent power when compared to other solvents, its boiling point, and its azeotroping characteristics.

Use of alternate materials in these industrial areas is often not a case of simple substitution, for technical or economic reasons. Use of an alternate material can sometimes not be made without causing process adjustments and/or increases in production cost.

4.1 ALTERNATE SOLVENTS IN CHEMICAL MANUFACTURING PROCESSES

Solvents are used as adjuncts in the manufacture of a large number of chemicals. For a given application, there are many potential alternate solvents.

However, in making substitutions, choices are influenced by the products, the impurities and the other system components, and each process and its requirements must be evaluated separately.

The main processes which may require a solvent adjunct are:

- Reaction solvents
- Azeotropic dehydration and distillation
- Extraction
- Recrystallization and purification

Where benzene is used as the solvent medium for a reaction, it may also be one of the reactants, as in its use in the Friedel-Crafts reaction. In polymerization reactions, for example, in the production of synthetic rubber, it may be used as a reaction solvent. Cyclohexane, toluene and xylene are the chief alternates to benzene in this application. For example, cyclohexane is being phased in as a substitute for benzene in one manufacturer's polymerization process for synthetic rubber. In many instances, substitutions may require process changes or adjustments.

Azeotropic dehydration/distillation is the major operation to use benzene in the manufacture of chemicals, and to be adaptable to the use of alternate solvents. Our current review of the industry has shown the following solvents to be the main choices for substitution: toluene, xylene, cyclohexane, and some esters, such as ethyl acetate. It is necessary that the alternative solvent be compatible with the system and not react with the components which are to be separated. The substitution of the solvents listed above often requires no major process change, only adjustments in temperature and flow rates. There is very little use of heptane and hexane as alternates to benzene as azeotroping agents.

Alternate solvents for extraction processes are selected on the basis of the product, the impurities, and their relative solubilities. Again, toluene, xylene and cyclohexane are used as alternates to benzene, as well as some aliphatics such as hexane.

Recrystallization and purification processes allow more freedom in the choice of alternates. Again, the properties of the product and its impurities are the chief considerations. Cyclohexane, cyclohexanone, toluene, xylene, ketones and naphthas may replace benzene for this use.

4.2 ALTERNATE SOLVENTS IN SPECIALTY CHEMICAL MANUFACTURE

For this area of chemical manufacture, the alternate solvents are more dependent on the end use of the product than in the case of general organic syntheses. Alternate solvents for each chemical will be reviewed separately, since they are used differently in each process.

4.2.1 Aluminum Alkyls

There are seven hydrocarbon solvents currently being used as alternates for benzene as packaging blend for aluminum alkyls. All serve to render the catalysts non-pyrophoric, and include hexane, xylene, heptane, toluene, isopars and cyclohexane. With the substitution of cyclohexane in the one remaining process which currently uses benzene as a solvent for a synthetic rubber polymerization reaction, benzene will no longer be used in the aluminum alkyl industry as a packaging medium.

4.2.2 Ethyl Cellulose Resins

Benzene was phased out as the process solvent for this application in 1976. Alternate solvents include toluene, ethanol and diethyl ether.

4.2.3 Alcohols

Solvents have two different uses in alcohol processing, one as a denaturant, and one as a dehydration agent. Once the pending OSHA standard is upheld, it is predicted that alternate solvents will have replaced benzene as a denaturant (1978 consumption is estimated at 2,000 gallons). Alternate denaturants depend on the end use, for example, industrial, pharmaceutical, the vinegar industry, and include toluene, methyl isobutylketone, methanol, gasoline, rubber hydrocarbon solvent, and ethyl acetate.

The use of benzene to dehydrate ethanol to the anhydrous finds limited alternate solvent choices due to the proportions of the azeotropic mixture formed. The companies that have changed solvents are using cyclohexane.

Alternate solvents for the dehydration of other alcohols (isopropyl and propargyl) are cyclohexane and isopropyl ether. Two anhydrous isopropanol producers have substituted alternates, and a third plans to do so.

4.2.4 Bisphenol-A

The use of benzene as an extractant for Bisphenol-A ceased in 1976. The substituted solvent was methylene chloride.

4.3 ALTERNATE SOLVENTS FOR RUBBER-BASED ADHESIVES

Elastomeric adhesives, both natural and synthetic, are soluble in a number of hydrocarbon solvents, and for most applications (see Section 3.4.2) adequate alternates have been found. These are discussed individually in this section.

In the tire manufacturing and retreading industries, special fractions of aliphatic hydrocarbons ranging from hexane to octane, and known as "Rubber Makers' Naphtha" or "Rubber Solvent" have been substituted for benzene. In some tackifier applications, phenolic resins or water-based rubber cements have been substituted, eliminating solvent use altogether. Petroleum naphthas, and aromatics such as toluene, have been substituted in the solvent adhesive package in tire and tube repair kits.

Industrial rubber products and rubber reclaiming operations do not use solvents of any kind.

Benzene is no longer used as a solvent in the elastomeric adhesives used in the footwear industry. Petroleum naphthas, toluene and xylene are the substituted solvents, or alternate adhesives such as hot melt adhesives or, in special instances, latex based adhesives are used.

Rubber-based "household cements" no longer contain benzene, with blends of toluene and naphtha being the main substitute.

4.4 ALTERNATE SOLVENTS FOR PAINT AND ALLIED PRODUCTS

Benzene has not been a component of paints for the last several years. Aromatics such as toluene and xylene, and petroleum distillate fractions have been the alternate solvents. In addition, there has been a significant shift in the market from solvent-based to water-based paints.

Paint and varnish removers are now blends of such materials as acetone, methanol, toluene, xylene, methylene chloride and naphthas.

4.5 ALTERNATE PROCESSES AND END PRODUCTS

Benzene as an adjunct to manufacture is used for its physical, rather than chemical reactant properties. The process technologies used in connection with benzene's employment as an adjunct comprise distillation, extraction, and crystallization, all based on the physical action of a solvent. Although the process technology is independent of the solvents employed, the reactants, and the impurities influence the choice of adjunct solvent. Process economics and equipment design may be adversely affected by the use of alternate solvents. Some adjustments in the process, such as temperature or flow rate are frequently required.

Processes for preparing a formulated product such as paint removers, adhesives and similar products are physical in nature. No chemical change occurs which would alter the character of the raw materials. Hence, the technology used to prepare these products is independent of the materials used in their formulation. The use of alternate chemical solvents in the preparation of the end product does affect selling price, and could change the effectiveness of the product.

The elimination of benzene as a solvent material in the paint and allied products field, the adhesive industry, and the rubber tire retread industry has not changed the overall effectiveness of the reformulated products.* However, price increases have resulted in several cases.

Table 4-1 summarizes alternate solvents currently replacing benzene for the consumption areas investigated in this report.

4.6 ENVIRONMENTAL MANAGEMENT OF ALTERNATE SOLVENTS

The environmental management for processes and methods which use benzene as a solvent does not change with the use of alternate solvents. The same precautions and methods of environmental control should be employed regardless of the solvent.

Proper maintenance of equipment, such as seals on pumps and agitators, is required to minimize losses. Spills and leakage on the floor or ground should be cleaned promptly either by flushing with water to a suitable liquid waste disposal system or adsorbed on material such as adsorbent clay for ultimate disposal.

Storage and process vessels should use control systems to minimize or eliminate air emissions. These systems may include vapor return between vessels, refrigeration to eliminate or reduce solvent vapors in vent gasses, or incineration. Liquid and solid residues containing solvent that cannot be recovered economically may be incinerated or buried in suitable landfills. Solvent contaminated air exhausted from the work place should be passed through a suitable gas adsorption system before being permitted to enter the atmosphere.

Again, the size of the establishment and type of process have a bearing on the economic resources which can be committed to pollution control. Adjunct chemical uses usually occur as part of large chemical operations, with well-developed environmental management programs. Pollution control for use of solvents in formulated products is less thorough and consistent, with most losses being vented to the atmosphere. Recovery here is more difficult technically, and less economic based on the volume lost compared to the volume consumed.

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* Discussions with industry spokesmen.

TABLE 4-1. ALTERNATE SOLVENTS FOR BENZENE

Application / Alternate	Cyclohexane	Toluene	Xylene	Heptane	Hexane	Cyclohexanone	Other Ketones	Ethyl Acetate	Naphthas	Methylene Chloride	Diethyl Ether	Ethanol	Methanol	Rubber Hydrocarbon Solvent	Other
Chemical Adjunct															
Reaction Solvent	X	X	X												
Azeotrope	X	X	X					X							
Extractant	X	X	X		X										
Recrystallization	X	X	X			X	X		X						
Aluminum Alkyls	X	X	X	X	X										Isopars
Ethyl Cellulose Resins		X									X	X			
Ethanol, Denatured		X					X	X					X	X	Gasoline
Ethanol, Anhydrous	X														
Other alcohols	X														Isopropyl ether
Bisphenol-A										X					
Solvent-type Rubber-based Adhesives		X							X						Hexane-octane blends; phenolic resins latex cements
Paints		X	X												Petroleum distillates
Paint thinners															Turpentine
Paint removers		X	X				X		X	X			X		

In terms of alternates for benzene, it can be seen from Table 4-1 that toluene is one of the most frequently used substitutes, particularly in high volume consumption areas such as chemical adjunct processes. There are various state and local regulations concerning the emission of photochemically reactive chemicals, such as Rule 66 in Los Angeles County and Regulation 5 in the San Francisco area. The State of Connecticut limits toluene emissions to 25 pounds per day. For formulators, the cost of reducing emissions to this level may be prohibitive. Thus, many industries may have to find substitutes for toluene, should this action be indicative of a trend.

SECTION V. SUMMARY OF BENZENE LOSSES

The consumption patterns of benzene as a solvent were discussed in Section 3 and are summarized in Section 3.6. In the context of this study, benzene consumption as a solvent represents losses resulting from its use as a process adjunct or as a component of a formulated product. The percentage losses are dependent on its application.

When the solvent is a component of a formulated product, the loss can be 100 percent during its ultimate use. When the solvent is used as an adjunct in a chemical process or in the manufacture of a formulated product, losses are estimated to be in the range of 1 to 10% of the volume in process, and are a result of:

(1) Fugitive losses from process equipment, storage and handling facilities and leakage from flanges, pumps, valves, etc.

(2) The solvent being a component of process waste streams.

The total volume of benzene circulated in those chemical processes which use benzene as a solvent adjunct can be calculated at any given time from overall consumption data. According to Table 5-1 approximately 4.8 million

TABLE 5-1. CONSUMPTION VERSUS ENVIRONMENTAL LOSS FOR BENZENE SOLVENT USES (1,000 gallons)

Consumption Area	Estimated Consumption		Estimated Environmental Loss	
	1976	1978	1976	1978
General Organic Synthesis	2,962	2,214	691	309
Pharmaceutical Synthesis	650	220	200	66
Small Volume Chemicals				
Aluminum Alkyls	312	312	312	312
Alcohols	465	100	225	55
Bisphenol-A*	0	0		
Ethyl Cellulose	0	0		
Formulated Industrial & Consumer Products				
Adhesives	0	0		
Rubber based adhesives	0			
Tire manufacture	0	0		
Tire retreading	0	0		
Industrial rubber products	0	0		
Tire patch repair kit	100	0	100	0
Miscellaneous				
Automotive	0	0		
Shoe	0	0		
Paints and Allied Products				
Paints and & Coatings	0	0		
Removers	300 to 500	0	300 to 500	150**
Total	4,789 to 4,989		1,828 to 2,028	892

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* Use in 1975 was 2,990,000 gallons

** Estimated amount in product made prior to May, 1977 and sold in 1978 gallons of benzene were "lost" in 1976, exclusive of the amount used in formulated products. This is equivalent to a nationwide consumption (or loss) of approximately 12,000 gallons per day. Assuming an average loss of 5%, the in-process volume can be estimated to be 240,000 gallons, exclusive of storage.

Overall losses of benzene resulting from its solvent applications are not equatable with environmental losses. These will be discussed in Section 5.1.

5.1 ENVIRONMENTAL LOSSES

Environmental losses to air, waste water systems and the soil occur as a result of the various solvent uses of benzene.

Air emissions result from:

(1) Evaporation of solvent from a formulated product during use

(2) Fugitive emissions from filling storage vessels, drums and equipment

(3) Fugitive emissions from process equipment and piping during its use and recovery as an adjunct in manufacturing operations

(4) Vaporization from waste water, liquid streams and solid wastes.

Liquid wastes are of two types:

(1) Waste waters from azeotropic dehydration processes in which benzene is soluble to the extent of about 0.07%

(2) By-product organic liquid streams contaminated with benzene.

Benzene loss to the soil is extremely rare. It can be due to the disposal of solids from filtration, crystallization or solid extraction processes.

Benzene's two distinct applications (chemical adjunct versus formulation or application) result in quite different emissions levels. This difference is due to the use of pollution control devices in integrated chemical plants which are usually not installed in non-chemical industries employing benzene as a solvent. There are no controls for any consumer oriented applications that might use benzene in the formulation.

Environmental control in an integrated chemical plant will take the following forms:

(1) A vent system to collect tank and process equipment emissions, conveying them to an incineration unit or an adsorption unit

(2) Waste water treatment plants

(3) Incineration of benzene-containing organic by-products or waste liquids

(4) Blending of benzene-containing organic liquid wastes into another process stream.

Chemical and pharmaceutical manufacturing companies that employ benzene as a solvent adjunct in chemical synthesis report make-up requirements at between 1 and 10% of the solvent circulated. However, because of the extensive use of pollution control equipment actual environmental losses may vary between 10 and 40% of the total benzene solvent make-up. The balance, 60 to 90%, is destroyed in the control processes.

Table 5-1 compares benzene solvent consumption estimates for the year prior to OSHA's proposed regulation, and that to be expected for the present (1978) year, with estimated environmental losses for both periods for each of the industrial and consumer applications.

5.2 GEOGRAPHIC DISTRIBUTION

Based on a review of benzene sales as reported both by distributors and producers, and by consumers, industrial benzene consumption as a solvent and environmental loss were in the following geographical areas in order of decreasing use (the remaining 2% was consumed at disperse locations):

West South Central	51%
Middle Atlantic	31%
East North Central	10%
East South Central	5%
West North Central	1%

Over 90% of solvent benzene is consumed and lost in connection with industrial processes. Environmental losses from these applications are concentrated at the industrial sites. The balance of the environmental losses occur with the use of consumer products which would be distributed more uniformly throughout the consuming area.

Figure 5-1 presents for 1976 the geographical distribution of benzene consumption as a solvent at industrial sites (including the manufacture of consumer products). This is shown as a percentage of the national consumption. Even though the actual quantity of benzene loss to the environment is less than the consumption because of the use of pollution control systems, the regional percentage losses will follow the same pattern.

5.3 TRENDS

Benzene consumption as a solvent, and therefore its environmental losses, have been decreasing at a steady rate. Its use in formulating consumer products has dropped to near zero following the issuance of the proposed regulation by OSHA and the concurrent issuance of a regulation by CPSC banning benzene in consumer products (Federal Register, 1978; OSHA, 1977).

Industrial uses of benzene as a solvent in such industries as rubber, rubber tires, automotive and adhesives have been non-existent, according to industry reports, for a number of years.

The major industrial solvent use area of benzene has been as an adjunct in the manufacture of chemicals, in pharmaceutical organic chemical synthesis and polymerization. Tables 3.1 and 3.3 show a more than 20% drop in benzene's use as a solvent adjunct in general organic chemical processes, including polymers, and over 60% drop in its use in connection with pharmaceutical synthesis between pre-OSHA 1976 and post-OSHA 1978.

Industrial spokesmen reported that they are investigating alternate solvents to benzene for its adjunct uses. In those cases where the processes permit the use of alternate solvents, the companies are making or planning to make the change.

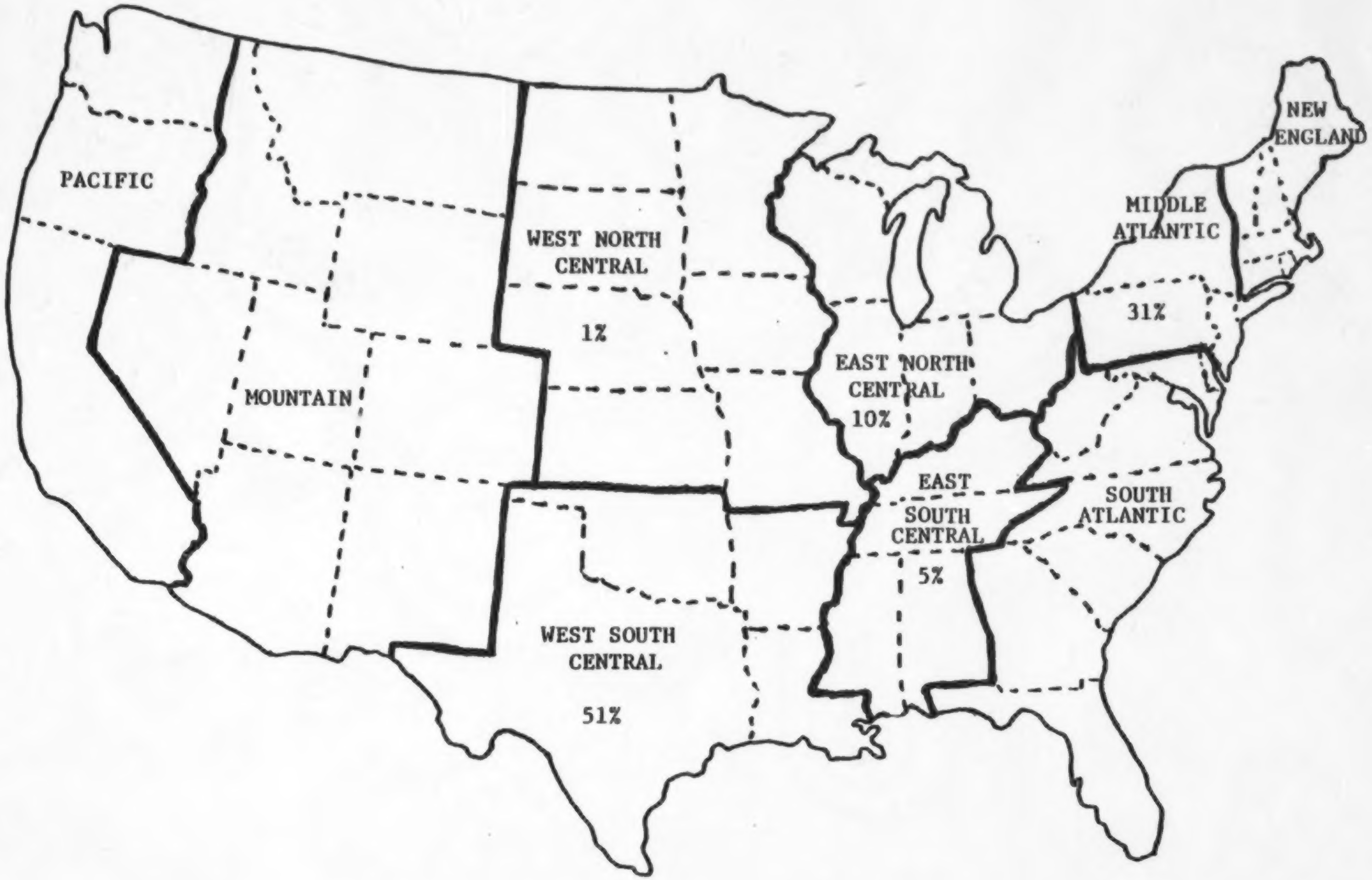
PACIFIC
MOUNTAIN
WEST NORTH CENTRAL
1%
WEST SOUTH CENTRAL
51%
EAST NORTH CENTRAL
10%
EAST SOUTH CENTRAL
5%
SOUTH ATLANTIC
MIDDLE ATLANTIC
31%
NEW ENGLAND

Figure 5-1. Geographic Distribution of Solvent Benzene Consumption by Region, 1976

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APPENDIX I. NOTES ON CALCULATIONS FOR TABLE 1-4

Ethylbenzene:

Calculated from styrene production

Conversion factors - Styrene from ethylbenzene - 1.17
Ethylbenzene from benzene - 0.76

Styrene prod. x 1.17 gives ethylbenzene consumed. Ethylbenzene must be adjusted for amount not made from benzene (i.e., from mixed xylenes). Find ethylbenzene capacity from mixed xylenes and multiply by plant operating rate for each year to get amount of ethylbenzene isolated from mixed xylenes.

$$\text{Operating rate} = \frac{\text{styrene production}}{\text{styrene capacity}}$$

Use styrene operating rate because ethylbenzene reporting is incomplete (styrene and ethylbenzene rates should be alike). Subtract ethylbenzene from mixed xylenes from total ethylbenzene. Multiply corrected ethylbenzene consumption by conversion factor, 0.76, to obtain pounds of benzene.

Cumene:

Conversion factor - 0.69

Cyclohexane:

Conversion factor - 0.93
80-85% of cyclohexane comes from benzene and the rest occurs naturally in hydrocarbon streams (Gunn, 1977). Take 82.5% of cyclohexane production and multiply by the conversion factor.

Chlorobenzenes:

Conversion factors - mono-0.82, di-0.62
Monochlorobenzene production figures are from USITC/USTC.
Di- figures for 1974, 1976, 1977 were calculated from mono- data, all others are from USITC. (Di- figures were not reported in 1974.) Calculations of di- data were made based on a di/mono ratio of .325, the average ratio for 1971, 1972 and 1975. 1976 - Di-figure was adjusted upward to .326 ratio because one company failed to report that year (Gunn, 1977).

Aniline:

Conversion factor - 0.9

Maleic Anhydride:

Conversion factor - 1.25
Beginning with 1975, increasing amounts of maleic anhydride were made from materials other than benzene. The amounts from benzene are: 1975-95%; 1976-92.7%; 1977-78%. These figures were calculated based on reported total capacity, newly built plants and plants converted from benzene feed (Gunn, 1977).

Alkylbenzenes:

Conversion factor - 0.4 (both)
Production data for branched alkylbenzenes is based on data for linear and calculated at a ratio of linear/branched = 2.64. Ratio is based on 1976 and assumed constant for all years.

Phenol (from Benzene Sulfonic Acid):

Conversion ratio - 1.0
Most phenol is produced from cumene. For phenol produced from benzene sulfonic acid, take 50% of phenol production from other than cumene.
Note: Reichhold Chemicals, the only company producing phenol via this route, closed its plant early in 1978.

Anthraquinone:

Use conversion factor of 1.37 and Vat Dye production to calculate benzene consumed for anthraquinone.

Nitrobenzene (not for aniline):

Conversion factor - 0.65
Assume 4% of total nitrobenzene is not used for aniline (Gunn, 1977).

Biphenyl, Hydroquinone, Resorcinol:

Use changes in benzene production as basis for calculation starting with benzene consumption for a base year. These uses were considered to exhibit little growth.

Biphenyl:

Base year, 1975 20,000,000 lbs. of benzene consumed

Hydroquinone:

Base year, 1976 3,000,000 lbs. benzene

Resorcinol:

Base year, 1976 30,000,000 lbs. benzene

APPENDIX II. LIST OF COMPANIES CONTACTED

The following companies were interviewed regarding their use of benzene as a solvent. AAI is grateful to them for their assistance and cooperation in the preparation of this study.

A & S Corp.
Abbott Laboratories
Able Industrial Products
Aceto Chemical Co., Inc.
Acme Hamilton
Acme Solvent Reclaiming, Inc.
Advance Finishes, Inc.
Air Products & Chemicals, Inc.
Akron Chemical Co.
Alabama By-Products Co.
Alcolac, Inc.
Alden Rubber Co.
Aldrich Chemical Co., Inc.
Alfa Div., Ventron Corp.
Allen Rubber Co.
Allied Chemical Corp.
Allied Oil
Alox Corp.
Alpine Aromatics International, Inc.
American Adhesives Products, Inc.
American Chemical Service
American Cyanamid Co.
American Hoechst Corp.
American Lacquer & Solvents Co. of Miami
American Oil & Supply Co.
American Recovery Co.
American Synthetic Rubber Co.
Ames Laboratories, Inc.
AMF Voit, Inc.
Amoco Oil Co.
Amsco Div., Union Oil Co.
Angeles Chemicals Co.
Ansul Chemical Co.
Apco Industrial Solvents Co.
Arapahoe Chemicals, Inc., Subs. Syntex Corp.
Arco Chemical Co.
Arco Industrial Corp.
Arenol Chemical Corp.
Aristo Laboratories, Inc.
Arivec Chemical Co.
Argo Chemicals, Inc.
Armak Co.
Armco Steel Corp.
Armstrong Rubber Co.
Arsynco Co., Inc.
Ashland Chemical Co.
Atlas Refining Co.
Atlas Rubber, Inc.
J.T. Baker Chemical Co.
Balboa Industries
Baltimore Paint & Chemical Co.
Barium & Chemicals, Inc.
Wm. M. Barr Co.
BASF - Wyandotte Corp.
Baxter Laboratories
Bearfoot Corp.
Bethlehem Steel Corp.
Better Monkey Grip Rubber Co.
Biochemical & Nuclear Corp.
Bofors America, Inc.
Borden Co., Borden Chemical Div.
Borden Remington Corp.
Borg-Warner Corp.
Bostik Div., USM Corp.
Bowes Pacific Corp.
Bowes Seal Fast Corp.
Bristol Labs, Inc.
Bucks County Solvents & Chemicals, Inc.
Buffalo Color Co.
Burroughs Wellcome & Co.
Burton Rubber Processing, Inc.
Butens
Calcasieu Chemical Corp.
Calsol, Inc.
Carolina By-Products Co., Inc.
Carroll, Ltd.
Carter Div., Dennison Mfg. Co.
Celanese Chemical Co.

Central Solvents
Centrix Corp.
Certified Coating Products, Inc.
CF & I Steel Co.
Charter Chemicals, Charter International Oil Co.
Chemetron Corp.
Chem-Fleur, Inc.
Chemical & Solvent Distillers Co., Inc.
Chemical Commodities, Inc.
Chemical Dynamics Corp.
Chemical Leaman Tank Lines
Chemical Samples Co.
Chemisphere Corp.
Chemol, Inc.
Chemtech Industries, Inc.
Chemway Corp.
Chevron Chemical Co.
Chromalloy
Ciba Pharmaceutical Co., Div. Ciba-Geigy Corp.
Cincinnati Milacron Chemicals, Inc.
Cities Service Oil Co.
City Chemical Co.
Classic Chemical
Clayton Chemical
Clifton Adhesive, Inc.
Coastal Chemical Co.
Columbia Cement Co.
Commonwealth Oil Refining Co., Inc.
Composition Materials Co., Inc.
Cone Solvents, Inc.
Conoco Chemicals Div., Continental Oil Co.
Converse Rubber Co.
Cooper Tire & Rubber Co.
Cordova Chemical Co.
Corson Rubber Products, Inc.
Cotler Distribution
CPC International, Inc.
CPS Chemical Co.
Crest Chemical Corp.
Crosby Chemicals, Inc.
Crowley Chemical Co.
CTC Organics
Curtiss Laboratories, Inc.
Cutter Laboratories
Cyclo Chemicals Corp.
Dan River, Inc.
Dart Industries, Inc., Aztec Chemicals Div.
Dayco Corp.
Dayton Tire & Rubber Co.
Deccofelt Corp.
Degussa, Inc.
Delta Solvents
Diamond Shamrock Corp.
Dion & Son
Dixie Cap Rubber Co.
Dixie Chemical Co.
Dow Chemical Co.
DuPont Co.
East Falls
Eastern Rubber Reclaiming Co.
Eaton Corp., Air Controls Div.
H.B. Egan Manufacturing Co.
El Paso Products Co.
Elan Chemical Co.
Electric Hose & Rubber
Eli Lilly & Co.
Emery Industries, Inc.
Enerchem International
Ethyl Corp.
Evans Chemetics, Inc.
Exxon Co. U.S.A.
Fairmount Chemical Co., Inc.
Famis
Faultless Div., Abbott Laboratories
Ferro Corp.
Finetex, Inc.
Firestone Tire & Rubber Co.
Florida Distillers Co.
Florida Solvents
FMC Corp.
Foster Grant, Div. American Hoechst
Fritzsche Dodge & Olcott, Inc.
GAF Corp.
Ganes Chemicals, Inc.
Gates Rubber Co.
General Chemical Corp.
General Electric Co.
General Sealants, Inc.
General Tire & Rubber Co.
Georgia-Pacific Corp.
The Gillette Co.
Glidden-Durkee Div., SCM Corp.
Globe Solvents

Glyco Chemicals, Inc.
Gold Shield Div., Detrex Chemical Industries, Inc.
Goodall Rubber
B.F. Goodrich Tire Co.
The Goodyear Tire & Rubber Co.
W.R. Grace & Co.
Grain Processing Corp.
A. Gross & Co.
Guardian Chemical Corp.
Gulf Oil Chemicals Co.
H & S Solvent Corp.
Haarmann & Reimer Corp.
C.P. Hall Co.
Hamblett & Hayes
Hardwicke Chemical Co.
Harrelson Rubber Co.
Hart Products Corp.
Haven Chemical Co.
W.W. Henry Co.
Hercules, Inc.
Heterene Chemical Co., Inc.
Hodag Chemical Corp.
Hoffman-LaRoche
Hooker Chemical Corp.
Houston Solvents
ICI United States, Inc.
IMC Chemical Group, Inc.
Independent Refining Co.
Inland Chemical Corp.
Inmont Corp.
Inolex Corp.
International Flavors & Fragrances
Intex Products, Inc.
Jefferson Chemical Co., Inc., Subs. of Texaco, Inc.
Jerdan Chemical Corp.
Johnston Distributors, Inc.
Joli Plastics & Chemicals
Jones & Laughlin Steel Corp.
Kalman Paint & Chemical Corp.
Kanoo, Inc.
Kay-Fries Chemicals, Inc.
Kelly-Springfield Tire Co., Subs. Goodyear Tire & Rubber Co.
Kemstar Corp.
Kerr-McGee Chemical Co.
Kex Products, Inc.
King's Laboratories, Inc.
Kraft, Inc.
Kravex Manufacturing Co.
Lindsey & Hall
Long Mile Rubber Co.
Lonza, Inc.
M & J Solvents
M & T Chemicals, Subs. American Can Co.
MacArthur Petroleum & Solvent Co.
Mackenzie Chemical Works, Inc.
Magichemical Co., Inc.
Magna Corp., Aquaness Chemical Div.
Mallinckrodt, Inc.
Malmstrom Chemicals
Mansfield Tire & Rubber Co./Inland Rubber Corp.
Marathon Oil Co.
Maryland Chemical Co., Inc.
Matheson Scientific Div., Will Ross, Inc.
Matlack
Mattiace Industrial Chemicals
May Co., Ltd.
Mazer Chemicals, Inc.
McBride Chemical Co.
McKesson Chemical Co.
Mellon Chemical Co.
Mercer Rubber Co.
Merck & Co.
Merichem Co.
Merril National Labs
Midwest Rubber Manufacturing, Inc.
Midwest Rubber Reclaiming Co.
Milliken & Co.
Mobay Chemical Co.
Mobil Chemical Co.
Monsanto Co.
John B. Moore Corp.
Mystic Tape Co., Div. Borden
Naarden, UOP Fragrances
Nalco Chemical Co.
Napp Chemicals, Inc.
Narco Corp.
National Solvent, Inc.
National Starch & Chemical Corp.
Nearpara Rubber Co.
N.L. Industries, Inc.
Nobs Chemical Co.
The Norac Co., Inc.
Norda, Inc.
Northern Petrochemicals Co.
Northwestern Chemical Co.
Norton Petroleum Corp.
Norwich Pharmaceutical Co.

Norwood Chemical Co.
Noury Chemical Corp.
Occidental Chemical Co.
Oil & Solvent Process Co.
Olin Corp.
Organon, Inc.
Pacific Chemical Laboratories, Inc.
Paeco Rubber Co.
Para-Chem
Parke Davis & Co., Subs. of Warner-Lambert Co.
Pasley Solvents & Chemicals, Inc.
Patch Rubber Co.
C.H. Patrick & Co., Inc.
PCR, Inc.
Pearsall Chemical Corp.
Pemaco, Inc.
Pemco Adhesives, Inc.
S.B. Penick & Co.
Pennwalt Corp.
Petrochemicals Co., Inc.
Pfizer, Inc.
Pharmacaps, Inc.
Pharma-Tech Industries, Inc.
Phillips Chemical Co.
Pickering Oil
Piedmont Chemical Industries
Pierce & Stevens Chemical Corp., Div. Pratt & Lambert, Inc.
Plough, Inc.
Polarome Manufacturing Co., Inc.
Polymer Application, Inc.
Polysciences, Inc.
PPG Industries, Inc.
Pressure Chemical Co.
Proctor & Gamble Industrial Chemical Div.
Prodyne, Inc.
Publicker Industries, Inc.
Purity Organics
PVO International, Inc.
Pyrazine Specialties
Quaker Oats Co.
Quintana-Howell
Railchem Div.
Randolph Products Co.
Red Devil
Reheis Chemical Co., Div. Armour Pharmaceutical Co.
Reilly Tar & Chemical Corp.
Research Products, Inc. of Alabama
J.E. Rhoades
Rho-Chem Corp.
Rhodia, Inc.
Richardson-Merrill Co.
Richmond Organics, Inc.
Riker Laboratories, Div. of 3M Co.
Roberts Solvent Co., Inc.
Robertson Trucking Co.
Robinson Wagner Co., Inc.
Rocson, Inc.
Rohm & Haas Co.
Rorer Pharmaceutical Co.
RSA Corp.
Ruan Transport
Saber Laboratories, Inc.
Santell Chemical Co.
SARAMCO-Samson Ray Materials Co.
Sartomer Industries, Inc.
Scher Bros., Inc.
Schering-Plough Corp.
Schrader Automotive Products Div., Scovill Mfg. Co.
Scientific Chemical Processing, Inc.
Searle Chemicals, Inc.
Shell Chemical Co.
The Sherwin Williams Co.
Siloo, Inc.
Skelly Oil (now Getty)
G. Frederick Smith Chemical Co.
Smith, Kline & French
Solvent Chemicals
Solvents Recovery Service of New England
Solvents Recovery Service of New Jersey
Southern Coast Chemical Corp., Gold Coast Oil Corp.
Southland Solvents & Chemical Co.
Southwestern Oil & Chemical Co.
Southwestern Refining Co.
Spencer Kellogg Div., Textron, Inc.
E.R. Squibb Co.
Stabond Corp.
StaLube, Inc.
Standard Chemical Products, Div. Henkel, Inc.
Stauffer Chemical Co.
Stephen-Roger, Inc.
W.H. Stevenson Co.

Stoney-Mueller, Inc.
Suburban Chemical Co.
Sun Oil Company
Sunkist
Superior Rubber Products Co.
Super-Tire
Swope Oil & Chemical Co.
Syntex Agribusiness, Inc.
Talon Adhesives Corp.
Tauber Oil
Tenneco Chemicals, Inc.
Texaco, Inc.
Texas Alkyls, Inc.,
  Div. Stauffer Chemical Co.
Texas Eastman
Texas Solvents
Textile Chemical Co.
Thiokol Chemical Corp.
31, Inc.
Thomas Solvent Co.
Thompson-Hayward
3M Co.
Tri-K Industries, Inc.
Triple R Industries
Tru-Flex Rubber Products Co.
Tumpeer Chemical Co.
Ungerer & Co.
Union Carbide Corp.
Union Rubber & Asbestos Co.
Union Rubber Co., Inc.
Uniroyal, Inc.
United Rubber Corp.
U.S. Industrial Chemicals Co.
U.S. Oil Co.
U.S. Pipe & Foundry
U.S. Rubber Reclaiming Co., Inc.
USS Chemicals Div., U.S. Steel Corp.
UOP Chemical Co.
Upjohn Co.
Van Waters & Rogers
Welch, Holme & Clark Co., Inc.
Western Eaton Solvents & Chemical Co.
Whitaker Oil Co.
Wilhold Glues, Inc.
Willard Tire Co.
Witco Chemical Co., Inc.
Wyeth Laboratories, Inc., Div.
  American Home Products, Inc.